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54 Biooxidation process for recovery of metal values from sulfur-containing ore materials.

57 A process for biooxidation of sulfides in a heap of mineral ores by freeing precious metals dispersed or occluded within said ores as pyritic or arsenopyritic sulfides and the like; the process comprises forming particulates from ore particles with an inoculate comprising bacteria capable of attacking, by biooxidation, sulfides and/or elemental sulfur in said ore particles; agglomeration aids may be used for forming particulates in conjunction with the foregoing which are acid resistant and not attacked by the bacteria; from these particulates a heap is constructed; and the biooxidation takes place in such heap by further adding to or dispersing within the heap the biooxidation solution and thereafter a leaching solution, circulating the leaching solution within the heap and recovering the precious metal values from the heap; recovery may be accomplished with a cyanide, thiourea, or a thiosulfate lixiviant.

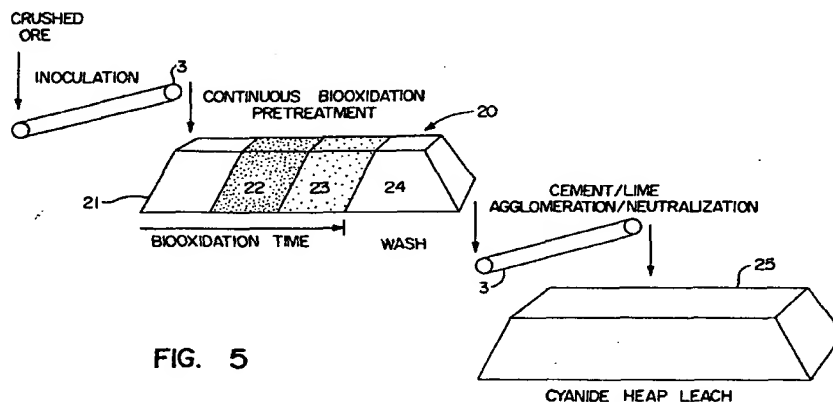


FIG. 5

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This invention relates to recovery of precious metals, e.g. gold and silver, from ores having a sulfidic sulfur and/or elemental sulfur content, such as sulfide-containing leachable ores of the pyritic, arsenopyritic, or arsenian pyrite type, refractory carbonaceous sulfide ores which have been pretreated, ores which are being post-treated, tailings, previously considered waste grade ores (which still have sufficiently high gold and silver content) and overburden ores having fairly low gold content and which may be considered waste ores.

This invention also relates to the recovery of non-precious metal values from ores having a sulfidic and/or elemental sulfur content whether as an incident to the recovery of precious metals or as a recovery of the nonprecious metals.

More particularly this invention relates to a specific treatment of particularly prepared ores of vast quantities and typically leached in heaps, dumps, tailing dumps, or waste dumps and the like. Still more particularly this invention relates to an ore treatment which starts with a preparation of particulates of specific design characteristics making the recovery of precious metals in low amounts and/or the recovery of nonprecious metals especially attractive and suitable for a heap or dump leaching, a construction of these specifically inoculated particulates and a heap or dump constructed from the specifically inoculated particulates suitable to an outstanding degree for biooxidation reactions with either single, mixed, layered, or staged biooxidant bacteria cultures.

Further, this invention relates to an especially suitable form of a biooxidized and treated ore used in subsequent downstream precious metal extractions, such as by thiourea, or, with or without heap reconstruction, by thiosulfate or cyanide extraction of the precious metal values in the ore heap or in subsequent downstream nonprecious metal extractions, such as by suitable lixivants, of the desired metal value(s) in the ore heap. Foremost amongst the ores being treated for precious metal recovery are gold ores. Foremost amongst the ores being treated for nonprecious metal recovery are copper, zinc, nickel, molybdenum, cobalt and uranium ores.

Typically precious metal containing ores are leached with cyanide as the most efficient leachant or lixiviant for the recovery of precious metal values from the ore. It would also be highly desirable to recover nonprecious metal values by heap leaching or lixiviation.

However, because of the mineralogy of various ores, access to the precious and/or nonprecious metal in the ore by cyanide or other lixiviant is low for an economical extraction of the precious metal and/or nonprecious metal values in an ore. If the cyanide extraction produces small or negligible amounts of gold, an ore is said to be refractory or highly refractory. Various methods have been employed to increase the extractability of the precious and/or nonprecious metals. A good summary article describing the prior problems is that authored by Kantopoulos et al., Process Options for Refractory Sulfide Gold Ores: Technical, Environmental, and Economic Aspects, Proceedings EPO '90 Congress, D.R. Gaskell, Editor, The Minerals, Metals & Materials Society, 1990.

A typical component which causes the refractoriness of the ore is predominantly a carbonaceous type component either inorganic or organic. The organic carbonaceous materials are also classified as acid insoluble carbonaceous materials. Gold found in ores dispersed within or occluded in a sulfide matrix may be considered refractory because of inaccessibility of such gold by cyanide leaching. Similarly, nonprecious metal values found in ores either dispersed within or occluded in a sulfide matrix or present as metal sulfides are also not readily recoverable by heap leaching or lixiviation.

When treating such ores, the economic considerations dictate the selection of the process or the pretreatment of the ore to render it amenable first and foremost to cyanide extraction even though other gold lixivants may be used. Similarly, it is highly desirable with nonprecious metal values in sulfidic ores to render them recoverable by heap leaching or lixiviation.

As one of the desired treatment steps prior to cyanidation or comparable lixiviation, roasting of ores in presence of air is typical. Lately oxygen or oxygen and air roasting, at low temperatures, have showed considerable promise. Other commercial ore treatment methods prior to cyanidation are high pressure oxygen and/or oxygen-ozone pretreatment, chlorine pretreatments, hypochlorite pretreatments and the like.

To improve cyanidation of ores during such cyanidation ozone, or ozone and oxygen, or oxygen, or a surfactant, or combinations of these are also employed. In the instance of gold recovery, methods such as "carbon-in-pulp" (or "CIP") and "carbon-in-leach" (or "CIL") are used to improve cyanidation reactions and gold recovery.

However, cyanidation has certain shortcomings, primarily an ore material must be neutralized after an acid generating treatment as cyanidation must be carried out on the alkaline side of the pH scale; likewise high cyanide consumption renders a process less attractive. When using thiourea, neutralization of the ore is not as demanding and does not affect thiourea extraction of gold, but the extraction economies are impaired by the higher cost of thiourea and the reduced efficiency when compared with cyanide.

Other compounds which have been used and offer promise because of reagent costs are compounds such as thiosulfates of which ammonium thiosulfate is one of the desirable candidates. Although still other materials are used for gold recovery, these are not yet of industrial significance.

When ammonium thiosulfate and the like are used, neutralization of ore is required as appropriate pH ranges are neutral to alkaline, e.g. to about pH 7 to 10 and preferably to at least about 9. As pyritic sulfidic ores and many other ores need to be neutralized because of the acidity of these ores when subjected to oxygenation or biooxidation and like treatments, separate process steps are required.

Inasmuch as gold is occluded in the sulfide matrix of the ore, the accessibility by cyanide has sought to be improved for these ores; the same is also true when considering an appropriate sulfide, e.g., pyrite for oxidation or biooxidation. Although various oxidation or biooxidation reactions have been tried such as vat, autoclave, slurry or liquid solution oxidations, these reactions are not practical when using large ore bodies having low gold content. As one of the approaches to oxidation of low content metal sulfide ores, biooxidation has come into prominence and much effort has been expended in research. Biooxidation was first applied to copper. Biooxidation of copper ore has been a well tried method although it is considered fairly slow.

When biooxidation is coupled with oxidative bioleaching, i.e. when direct, indirect and even galvanic leaching reactions are involved, some of the disadvantages of the slow biooxidation reactions are mitigated. Biooxidation reactions typically involve arsenopyritic and pyritic iron sulfide-containing ores including those that have some refractory carbon components present. Biooxidation, however, can suffer from inhibitory concentrations of some metals present in the ore. Biocidically active metals are such as arsenic, antimony, cadmium, lead, mercury, molybdenum. Ions such as chlorine, bromine and the like affect the biooxidation processes. Because of slow growth rates for some bacteria as well as temperature variations in a typical ore dump undergoing sulfide oxidation, considerable efforts have been expended to improve the rate constraints which have limited or held back the potentially very useful application of biooxidation.

Hence, considerable investigation has been made of the various limiting conditions concerning commercial biooxidation including such factors as ores in heaps or in slurry form, the use of surfactants, the use of potentiators or biooxidation promoters such as silver, aluminum, etc., appropriate selection and growing of robust bacteria which would be resistant to the inhibitory biocide activity of metals such as arsenic and growing the bacteria in profuse amounts. Other considerations have been such as nutrient access, air access and carbon dioxide access for making the process even more efficient and thus an attractive ore treatment option. References illustrating these efforts are such as by Bartlett, Aeration Pretreatment of Low Grade Refractory Gold Ores, Minerals and Metallurgical Processing, pp 22-29, (Feb. 1990); Bennett et al, Limitations on Pyrite Oxidation Rates in Dumps Set By Air Transport Mechanisms, Biohydrometallurgy, Proceedings of Jackson Hole Symposium, August 13-18, 1989 Canmet (1989); Burbank et al, Biooxidation of Refractory Gold Ore in Heaps, Ch. 16, pp 151-159 in Advances in Gold and Silver Processing, Reno Proceedings of Symposium "Goldtech 4", Reno, Nevada, September 10-12, 1990, Society of Mining, Metallurgy and Exploration, Publisher, 1990; Dix, Laboratory Head Leach Testing: How Small and Large Scale Tests Compare, Mining Engineering, June 1989, Pages 440-442.

Amongst the methods seeking to improve biooxidation many methods have been proposed for mechanically increasing the access of the biooxidant bacteria to the ore. These methods have relied upon agitation of the ore either in tanks, slurries, providing circulation in vessels or reconstitution and remixing of the materials including stirring, raking, forming an improved slurry, transfer of slurry materials, providing stirred tank basins or have addressed various aspects of heap construction and utilization. References to such considerations are found in an article by Andrews, Large-Scale Bioprocessing of Solids, Biotechnology Progress, Vol. 6, pp 225-230, 1990.

Patents which illustrate some of these methods mentioned above are found such as in U.S. Patent No. 4,324,764 concerning mechanical distribution of ores or distribution of ores by conveyors such as in U.S. Patent No. 4,571,387 or a change in heap structure such as in U.S. Patent No. 4,279,868 or stagewise heap formation such as in U.S. Patent No. 4,017,309; or a stirred tank - semi "heap" construction such as disclosed in U.S. Patent No. 4,968,008.

However, when treating large amounts of waste heap material or tailing material, the normal considerations that are applicable in high grade precious metal ore treatments are not viable. For waste ore treatment, economics often dictate a one-shot type of heap formation, e.g. for the depth, the size, the reactant accessibility, etc. Moreover, for biooxidation, the induction times concerning biooxidants, the growth cycles, the biocide activities, viability of bacteria and the like become important because the variables such as accessibility, particle size, settling, compaction and the like are economically irreversible once a heap has been constructed as such heaps cannot be repaired except on a very limited basis. For example, compaction problems such as are encountered in heap treatment of ores, and others such as

puddling, channelling, or nutrient-, carbon dioxide-, or oxygen-starving, uneven biooxidant bacterial distribution, and the like have been addressed in a number of investigations with respect to biooxidation. Such problems are also encountered in cyanide leaching.

For example, to solve channelling in percolation leaching by cyanides it is known to agglomerate the ore materials of high grade ores such as disclosed in U.S. Patent No. 4,256,705 and 4,256,706. Other approaches to improve percolation leaching by cyanides include addition of fines such as flocculating materials, fibers, wood, pulp and the like as disclosed in U.S. Patent No. 4,557,905. The last patent discloses leachable matrix formation to allow for access of cyanide to the precious metal values.

An ultimate, albeit impractical, suggestion for cyanide leaching has been found in U.S. Patent No. 4,424,194 which shows making useful articles and then leaching these. This patent may have as its progenitor the early U.S. Patent No. 588,476 of August 17, 1887, which discloses porous casts made of gold "slimes" and gypsum. These casts are thereafter broken and leached.

Although for a variety of different reasons agglomeration has been practiced in the metallurgical arts such as in high temperature blast furnace art for various feed material preparations for blast furnaces, opposite suggestions have also been found concerning non-agglomeration and extraction of metals such as the pulp-liquid extraction described in U.S. Patent No. 3,949,051. Extraction of the precious metals from heaps, preformation of heaps and heap treatment is found such as in U.S. Patent No. 4,017,309 and 4,056,261.

Further improvements for access of cyanide to the precious metals have been described in U.S. Patent No. 4,318,892 and 4,279,868 as well as U.S. Patent No. 4,301,121. All of these attempts have sought to improve the distribution of the leachant or the mixing ratios of the ore to the lixiviant, but these attempts are typically addressed to providing better access for cyanide and to overcome the ostensible refractoriness of the ore. Other like disclosures have been found in U.S. Patent No. 4,324,764 and 4,343,773.

Heap improvements have been found in the construction of the particles such as paste formation with the lixiviant and subsequent ageing of the ore on treatment of the same, described in U.S. Patent No. 4,374,097. Likewise, specific berm construction for the improved extraction of liquids from a specifically constructed heap has been found in U.S. Patent No. 4,526,615. Similarly various particle specifications have been described for the ore particle treatment including the micro agglomerates of a size of 500 microns (and lower) found in U.S. Patent No. 4,585,548.

In all of these heap formations, heap treatments or heap leaching methods, shortcomings have been sought to be overcome by the increase of cyanide efficiency such as by oxygen addition, e.g. in U.S. Patent No. 4,721,526, or the use of various liquors in the recovery of gold described in U.S. Patent No. 4,822,413.

Agglomerating agents for copper ores are shown in U.S. Patent No. 4,875,935. Opening up clogged heaps has also been shown and discussed in U.S. Patent No. 3,819,797 and heap treatment for distribution of a lixiviant is disclosed in U.S. Patent No. 5,005,806. Finally, both conjoint crushing and agglomeration of ore has been discussed in U.S. Patent No. 4,960,461.

Attempts have been made to ameliorate the compaction and imperviousness that results when ore materials containing clays and/or fines are heaped. Clays and fines pose difficulties in hydrometallurgical processes used in the recovery of metal values from ore materials. In order that an inappropriate accumulation of clays and fines does not hinder the flow of process liquor through a heap of ore material during heap leaching, clays and fines need to be immobilized and uniformly distributed in the heap, such as by agglomeration with larger particles of ore material. Unfortunately, the percolation of process liquor through the heap has a tendency to free clays and fines from the agglomerate and to result in the segregation of clays and fines from agglomerates and their migration into a nonuniform distribution in the heap. This loose clay and fine material can concentrate in pore spaces and plug flow channels in the heap. In addition, the pH of the environment in the heap can exacerbate this problem since pH has an effect on the swelling of clays and the stability and solubility of components of the ore material. In this regard, see Kurtz, J.P., et al. *Clay Problems Encountered in Gold Heap Leaching* (manuscript submitted to Society of Mining Engineers for the Symposium on "Small Mines Development in Precious Metals" August 30 - September 2, 1987) and Chamberlin, P.D., "Agglomeration: Cheap Insurance for Good Recovery When Heap Leaching Gold and Silver Ores", *Mining Engineering* 1105-1109 (December 1986.)

One attempted solution to this problem is the addition of cement as a binding agent and lime as a pH control in caustic cyanide leaching environments resulting in a high heap pH. While a high pH itself poses problems with respect to swelling and undesired solubilization of minerals, biooxidation requires an acid pH - an environment at odds with the pH produced by the cement/lime approach to agglomeration.

Anionic copolymers of acrylamide and acrylic acid have been used as described in U.S. Patent Nos. 5,077,021 and 5,077,022 as agglomerating agents in heap leaching with caustic cyanide leachants - a

strongly alkaline environment that is inhospitable to biooxidative microbes, such as *Thiobacillus ferrooxidans*. Reconstituting an ore heap in order to agglomerate the ore material with an alkali-tolerant agglomeration aid before caustic cyanide leaching is not as economically efficient as being able to prepare a heap, decrease its sulfide refractoriness and then leach desired metal values - without needing to reconstitute the heap to change agglomeration agents.

U.S. Patent No. 3,418,237 issued December 24, 1968, describes the use of water-soluble acrylic polymers in settling ore pulps that contain only up to 25% clay. The described polymers are stated to be completely ineffective in settling mineral suspensions when the amount of clay materials present exceeds about 25%.

U.S. Patent No. 4,875,935, issued October 24, 1989, discusses the use of anionic poly(acrylamide) polymers, including poly(acrylamide) copolymers with acrylic acid, methacrylic acid and itaconic acid, in the agglomeration of copper ores for heap leaching with dilute sulfuric acid. However, this approach ignores the issues raised by microbial biooxidation and microbial viability.

U.S. Patent No. 4,898,611, issued February 6, 1990, discusses the use of water-soluble vinyl addition polymers, such as poly(acrylamide) and its water-soluble acrylic acid, methacrylic acid, itaconic acid, acrylonitrile and styrene copolymers including cationic and anionic polymers, as agglomeration agents for heap leaching with a cyanide lixiviant. In this regard this approach is subject to the same deficiencies as U.S. Patent Nos. 5,077,021 and 5,077,022 discussed earlier.

The present invention relates to an improvement for the recovery of desired metal value(s) from an ore material comprising those desired metal value(s) and a matrix material having a sulfur content wherein the sulfur is present in an oxidation-reduction state of zero or less, but more typically such as sulfidic and/or elemental sulfur. The ore material also comprises clays and/or fines. The process of the present invention comprises the use of an acid-resistant, microbial biooxidant-compatible, water-soluble vinyl addition polymer agglomeration aid in the context of a process comprising

optionally adjusting the pH of the ore material to a pH of less than 2.5, separately or conjointly with acid solution-caused partial agglomeration,

forming particulates from particles of the ore material with an inoculate comprising microbial agent(s) capable of at least partially biooxidizing the sulfur content,

forming a heap of said particulates,

biooxidizing the sulfur content in the matrix and

recovering the desired metal value(s) either from the biooxidizing solution leachant or a specific leachant for the desired metal value.

The present invention further relates to said particulates and to heaps formed of said particulates. The terms "ore" or "ore material" as used herein includes not only ore per se, but also concentrates, tailings or waste in which sufficient metal values exist to justify recovery of those values.

The desired metal value(s) may be selected from

Group IB metals of the periodic table of elements (CAS version)

(copper, silver, and gold);

Group IIB metals

(particularly zinc);

Group IV A metals

(germanium and lead, particularly lead);

Group VA metals

(particularly arsenic and antimony);

Group VIB metals

(chromium, molybdenum and tungsten, particularly tungsten);

Group VIII metals

(iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium and platinum, particularly, nickel, palladium and platinum) and

The Actinide series metals

(particularly uranium).

Preferred among these metals are copper, silver, gold, zinc, cobalt, nickel and uranium. Gold is the most desired metal in the above group.

The matrix material, in addition to having the described sulfur content, may comprise one or more inorganic metallosulfur compounds in which the sulfur moiety conforms to the description of the sulfur content and the metal moiety comprises a metal as previously described. Examples are as follows:

| | |
|--------------|-----------------------------|
| Arsenopyrite | FeAs_2S |
| Bornite | Cu_2FeS_4 |
| Chalcocite | Cu_2S |
| Cobaltite | CuFeS_2 |
| Enargite | Cu_3AsS_4 |
| Galena | PbS |
| Greenockite | CdS |
| Millerite | NiS |
| Molybdenite | MoS_2 |
| Orpiment | As_2S_3 |
| Pentlandite | Ni_9S_8 |
| Pyrite | FeS_2 |
| Pyrrhotite | $\text{Fe}_{1-0.8}\text{S}$ |
| Sphalerite | ZnS |
| Stibnite | Sb_2S_3 |

- In this context, the desired metal value(s) may be present in the ore material either as
1. an elemental metal, such as gold, dispersed within or occluded in the matrix material;
 2. a compound, such as a metal oxide, dispersed within or occluded in the matrix or;
 3. a component of the matrix material, such as a metal sulfide.

The present invention renders such desired metal values accessible to recovery treatment in the sense that biooxidation of the sulfur content either exposes the elemental metal or compound for further recovery treatment or it also renders the desired metal values soluble or otherwise accessible to recovery treatment.

The present invention has preferable value in the recovery of gold from low gold content gold ore materials having a sulfidic sulfur content and more desirably in those instances where the matrix material comprises an iron-sulfur compound. Of particular interest are low gold content refractory pyritic and arsenopyritic gold ores.

In none of the references described in the Background of the Invention, relating either to the first stage bacterial biooxidation or the coupled second stage downstream cyanide or like extraction has there been a disclosure for forming specific particulates with a bacterial solution as suitable for low metal content ores treated in a heap; as well as for the biooxidation of low content gold ores. By "low" it is meant a gold-containing ore of less than about 0.07 oz/ton of ore. (While the present invention will be described in terms of its desirability in recovering gold from such low content gold ores, it should be understood that it has application to the previously described metals in other levels of metal value content.)

The invention has particular applicability to ore materials with a high clay and/or fines content. Clay particles can migrate through the heap and, upon swelling and lodging in the channels between ore particles, plug those channels. Fine particles (50 wt% -200 mesh) similarly can migrate through the heap and, by accumulation, block percolation channels in the heap. This creates zones in the heap of lower permeability to percolating process liquids. Such ore materials prove difficult to treat by heap leaching or other heap liquid percolation techniques because the clay and/or fines compact and plug the liquid channels in the heap, preventing facile circulation of process liquor through them. This impairs uniform processing of the constituent particles of the heap since the circulating liquid is unable to reach those particles uniformly, leaving some starved of process liquor and, hence, processing. This produces lower extraction, longer leach time and higher reagent consumption.

One measure of the efficacy of an agglomeration aid in preventing the migration of clays and/or fines from particulates into a heap and the resulting increased resistance to solution flow the rate of percolation of solution. In percolation rate testing a cylindrical column is loaded with a test sample and the percolation rate is measured. Each sample is prepared so as to retain constant conditions from sample to sample, such as moisture content, particle size, particulate size, clays and/or fines to solids ratio, particulate surface area, etc., the only variable being the presence or absence and amount of the agglomeration aid being tested.

This permits various agglomeration approaches to be compared accurately. The column is loaded with a specified volume of prepared sample to a specified height. The percolation solution is added to a fixed head and the percolation solution is circulated through the column for a specified period of time while maintaining the head at the specified level. At the end of the specified period of time the percolation rate is measured and evaluated - a lower percolation rate indicating that the clays and/or fines have migrated from their original particulates and plugged flow channels.

Another measure of the efficacy of agglomeration aids in preventing migration is direct measurement of the amount of clays and/or fines at various levels in a simulated heap. The equipment and technique are the same as for the percolation rate testing except that, instead of measuring percolation rate, at the end of the specified time period specimens are taken at specified depths in the column and each specimen is analyzed for its clays and/or fines content. The percentage of clays and/or fines at each depth with respect to the total clays and/or fines content would indicate the deviation from a uniform distribution, i.e., one in which the clays and/or fines were still attached to their original particulates and, hence, had not migrated.

With respect to actual heaps in the field, the efficacy of an agglomeration aid to prevent migration can be generally determined by observing whether or not there are regions of the heap where there are visible accumulations of percolation solution.

By the term "particles" it is meant the individual particles found in the ore such as run-of-the-mine ore; further, it is meant, ore particles formed after either primary or secondary grinding or crushing; by the term "particulates" it is meant the body or shape which is built up from the individual particles properly coated with an agglomeration agent as described herein prior to, conjointly with or subsequently to wetting the particles with an inoculant solution(s) containing bacteria; or an agglomeration agent as described herein used according to the same schedule as the inoculant solution but constructing the particles from a sulfuric acid-containing solution followed by an inoculant solution containing a specific bacterium or bacteria of a specific undifferentiated strain or a mixture of bacteria. Such particulate design, construction or formation and the concomitant heap construction have especially desirable properties for the reactant, i.e. the biomass distribution, dispersal and access to: a) the metal values in an ore, particularly low-concentration metal values, or b) low sulfide and metal, particularly low-concentration metal values in an ore. None of the references discloses an economically attractive method for improving the proper initial construction of a heap, for biooxidation purposes, as well as to provide for a more efficient method e.g. cyanidation, for precious metal recovery downstream after biooxidation has taken place in the initially, properly constructed heap.

In its essential aspects, the present invention is directed to a biooxidation stage of an ore in the form of particulates with various pre-treatment and post-treatment steps related to the biooxidation. A subsequent precious metal recovery stage for extracting the precious and/or nonprecious metals from the biooxidized ore body is made now more advantageous because of the initial formation of the ore particulates especially high clay content ore particulates with an acid- and bacterial action-resistant agglomeration aid of the described type with a bacteria coating which, as a result of improved biooxidation, makes the ores now especially amenable for the subsequent recovery, such as by cyanide or other extraction, of the desired metal value(s) from such biooxidized ores. Further, the appropriate agglomeration agents of the invention facilitate the biooxidation and, preferably, the subsequent recovery of metal values.

In accordance with the invention, a combination of steps is proposed which has interrelated a number of variables and has sought to reduce the rate limiting conditions for metal ore materials, especially for low precious metal content ore materials heretofore considered wastes and heretofore not capable of treatment for recovery of the precious metals therein because of rate limiting conditions imposed by high clay content ores due to permeability loss from stripped clay particles such as in biooxidation of low, medium and high clay content, low sulfur content gold ores. By low sulfur content it is meant ores of less than about 0.2 to 0.3% sulfide by weight. While the present invention, has been described with respect to low sulfur content with respect to the recovery of precious metal values such as gold, it is also amenable to use with higher sulfur content ores. By low clay content ores it is meant ores with clay content less than about 5 weight percent; by medium clay content ores it is meant ores of clay content of less than about 20 weight percent; by high clay content ores it is meant ores of about 30 weight percent and more of clay.

Thus, in accordance with the present invention and its preferred mode, waste materials having a gold content as low as 0.07 oz/ton and even as low as 0.02 oz/ton of gold in an ore may now be economically treated for recovery of the precious metal values. A preferred range is for ores of a gold content above 0.02 oz/ton of ore. Of course, the precious metal values, such as gold, in the ores significantly above the indicated threshold values are also recoverable but other means or options provide fairly attractive and economically competing alternatives which make the present process only a matter of choice in circumstances where such choice needs to be made.

Thus, it is considered practical in accordance with the present invention to treat tailings, waste material, or low grade overburden or previously exhausted dump material if the precious metal values in such ore bodies are at or above 0.02 ounces of gold per ton of ore or the monetary equivalent thereof in case of gold and silver or silver alone; if the ore is treated on the acid side of pH at a pH from 1.5 and above; if the ore
 5 contains clay materials of greater than about 10 weight percent; and if the ore has been agglomerated with the proper acid -resistant agglomerating agents.

Still further, it has been found that the discovery, as disclosed herein, makes the process especially amenable to the low grade ores as a heap or dump treatment, with outstanding recovery rates for the metal values in the ores despite the presence of clay in the ore if these ores are subjected to the herein disclosed
 10 method.

For example, the present invention contemplates the proper agglomeration of a distribution of fine and coarse ore material with considerable clay content with the concomitant proper distribution of the biooxidant bacteria.

It is to be understood that within the body defined by the heap, particulates of different size
 15 characteristics and distribution are also contemplated as being an attractive feature of this invention, especially to provide for access to regions previously considered "dead" regions in a heap and now made accessible by the present process.

The above ore material particulates when properly formed and distributed in a heap provide the advantages because the agglomerated inoculant-biooxidant material is appropriately made to contact the
 20 individual particles and/or the smaller particles are appropriately layered on the larger particles to form the particulates. It is to be noted that agglomeration solely with the agglomerating agent is only one of the methods for proper particulate formation and other equivalent methods shall become evident from the description of the desired particulates. Within such formed particulates or layers thereon are found the well established flora across the spectrum of the materials and thus the fine ore material particles provide an
 25 extremely attractive distribution of bioreactant bacteria over the entire ore body in a heap as defined by the various particulates formed also from unwanted, very small size particles such as clays and other very small size particles called "slimes" which may be of different constituents in admixture with larger particles. The same and different bacteria may now be introduced in an appropriate location if dictated by temperature, pH, biocide, access, water drainage (i.e. water saturation) and like considerations. Further, this invention
 30 also concerns itself with proper particulate formation by agglomeration from crushed ores which are being heaped on a dump heap at the same time as these particulates are treated with an inoculant liquor containing the suitable bacteria for particular layers in a heap.

Other and various inoculation/particulate formation features of this invention will be disclosed in conjunction with the formation of the heap and the distribution of the biooxidant bacteria throughout the ore
 35 mass and the heap.

In connection with the above, pretreatment steps may be practiced such as acid treatment with sulfuric acid to neutralize or partially neutralize high acid consuming ores (thereby partially also agglomerating the ores), followed by the agglomerating aid treatment of the ore and the further inoculation and particulate
 40 formation and distribution of the biooxidant bacteria throughout the ore mass as it is being treated for deposition on a heap.

In accordance with the invention, the particulate formation and the surface covering of the particulate with and the biooxidant bacteria distribution throughout are now achieved in an highly desirous fashion. These features provide for an extremely advantageous access of the bacteria to the sulfide matrix in the ore in various size particles of the ore as well as for the rapid growth and multiplication of the bacteria. The
 45 preferential attack on pyrites, such as arsenic pyrites (arsenopyrites and/or arsenian pyrites) and the tailoring and design of subsequent or supplemental biooxidant leachant solutions now give a number of options to devise an optimum treatment for a particular ore.

Because of the possibility to have mixed biooxidant bacterial ore particulates in a heap, the ability to layer a heap, and to add various types of bacteria at various points in the particulate formation, the process
 50 provides for flexible and tailor made heap constructions. This flexibility also holds true for layering sequentially or conjointly with mutually compatible bacteria, thus offering different advantages and capabilities with respect to the ore material being treated, e.g. consortia for attacking other components in the ore, e.g. acid insoluble carbon. In this regard, reference should be made to the microbial agents and their method of use described in U.S. Patent Application Serial No. 07/750,444, filed August 20, 1991, the
 55 disclosure of which is incorporated herein by reference.

Thus various bacteria that have outstanding characteristics for treating or materials containing biocidally active metals, such as arsenic, antimony, cadmium and the like, in large quantities in conjunction with iron which is present, have provided for an advantageous intermixing of various cultures and at various

points in the treatment cycle and in the heap body.

As a consequence of these advantages, short induction periods for growth have been experienced, better air and carbon dioxide accessibility provided, better nutrient infusion or supplementation practiced, more bio-mass is maintained throughout the heap, compacting and/or clogging especially of high clay type ores are minimized, outstanding permeability is achieved, better percolation is achieved, puddling and/or channelling are minimized, water logging is avoided etc., etc. These and other advantageous features make the process very attractive due to the novel particulate design and heap construction resulting in an outstanding method for recovery of desired metals from metal ores, particularly precious metals from low content precious metal ores.

As one of the outstanding advantages of this invention, the first stage treatment steps carried out at acid conditions with the specified agglomeration aids have provided for down stream advantages for the recovery of the desired metal values, such as by a second stage, i.e. the cyanide or other lixiviant treatment for the extraction of the metal values or by recovery directly from the bioleaching solution. These second stage advantages result from, inter alia, improved porosity associated and achieved as a result of the agglomeration aid not being affected by bioleaching, good permeation of lixiviant minimizing of problems caused by clay stripping from the particulates, etc. Other advantages are such as: relatively fast rate of extraction; a heap treated ore of outstanding accessibility to the cyanide material or other lixiviant or the bioleaching solution itself; reduced cyanide/lixiviant/bioleachant consumption; and other heap type advantages, e.g. regeneration of the lixiviant; flexibility to meet variations in the treatment; an ability to neutralize more easily a heap (if such is desired); the reduction of the neutralization requirements because of the attractive wash cycles (which have been found to exist as a result of the first stage heap treatment with the biooxidant material); and, other and further advantages mentioned herein.

Consequently, as one of the features of this invention, the reconstitution of the heap for cyanide treatment or other lixiviation has become either unnecessary or economically attractive with the dispersed porous biooxidized matrix allowing for washing and attractive neutralization of the acidic heap material for the subsequent cyanidation or other lixiviation of the ore.

These and other advantages have further manifested themselves e.g. in that cyanocide fungi and other cyanide degrading microorganisms can now be readily used for the post treatment of the exhausted heap such as found in the disclosure in U.S. Patent No. 4,402,831. The improved intra particle and inter particle accessibility allows cyanide elimination.

With reference to the figures herein:

Figure 1 shows a conveyor belt type of assembly for agglomerating particles of the desired characteristics for the formation of particulates in a heap for subsequent biooxidation and leaching of the metal values;

Figure 2 illustrates a cross sectional area of an ore particulate made according to the illustration in Figure 1;

Figure 3 is self-explanatory and shows for a representative ore the difference in results for the ores treated in accordance with the present invention as against ores treated according to a conventional process i.e., where the ore is biooxidized by spraying thereon a bacteria-containing solution.

Figure 4 is self-explanatory and depicts the advantages of the present invention based on the rate of extraction of iron from two samples of the same ore.

Figure 5 illustrates schematically an embodiment of the present invention with respect to a heap of ore material being biooxidized and thereafter being reconstructed and cyanide treated;

Figure 6 illustrates another embodiment of the invention with respect to a heap of ore material being biooxidized in a "race track" fashion; and

Figure 7 illustrates a schematic of another embodiment for biooxidation leaching of an ore heap as well as a method for lixiviant and other solution management.

Referring to Figure 1 in the drawings, a belt system is shown comprising a hopper 1 in which sulfide ore 2 is confined. The ore is fed onto an upwardly inclined conveyor belt 3 having a spray system 4 cooperatively associated therewith.

Conveyor belt 3 is arranged in overlapping tandem relationship with upwardly inclined conveyor belt 5 which in turn it is arranged in overlapping tandem relationship with steeply inclined conveyor belt 6 from which particulates, gradually forming on the conveyor belts 3, are discharged at 7 to form heap 8.

In Figure 2 a cross-sectional area of a particulate 9 is illustrated. As shown, individual particles 10 are covered with a bacterial coating 11. As each ore has different fracture characteristics, e.g. for ground or crushed or even run-of-the-mine particles, it is clear that various particles 10 will appear in these ores in different form. Clay particles tend to be finer and smaller and are generally on the surface of the larger particles. It is to be noted that while the exact mechanism is not known for the formation of the particulates,

these particulates are sufficiently strong and resist significantly any compaction and/or resist being crushed in a heap by the weight of the material above the particulates. Moreover, clay particles resist lixiviant stripping of these from the particulate. Typically for sulfide ores, the particulates should be about 1 inch (25,4 mm) and less with about 45% to 50% of the sulfides in the particulate being oxidized. An optimum size for sulfidic ores is about 1/2 inch (12,7 mm) to about 1/4 inch (6,3 mm) allowing about 80% of the sulfides to be oxidized, (depending, of course, on the allowed time period.) However, the clay particles are smaller and, therefore, need to be agglomerated and bound to the particulates or formed into particulates.

For carbonaceous sulfidic ores, the size of the particulate should be about 1 1/2 inches (38,1 mm) and less with about the same amount of sulfides being oxidized as for the sulfidic ores. The optimum lower end of the size range is about the same as for sulfidic ores.

For cyanidation, the particulates should be about 1 inch (25,4 mm) -and less.

Figures 3 and 4 illustrate appropriate improvements in rate limiting conditions according to the present invention and as to typical conditions encountered in the prior art.

Thus gold extraction is improved as shown in Figure 3. The fast initiation and induction of a biooxidation for the invention herein is demonstrated by the rate of iron extracted as shown in Figure 4 for the depicted, overlapping biooxidation/extraction periods.

In Figure 5, a heap formed in accordance with the present invention is shown as 20. Heap 20 has an "induction" section 21 which is being freshly formed and represents schematically a lag time before a substantially significant biooxidation reaction starts. Section 22 of heap 20 illustrates schematically the heap in its most active biooxidation stage. Section 23 illustrates the heap in its mature biooxidation stage and corresponds schematically to a period during which a target biooxidized sulfide content in the ore is achieved. After that target has been reached, Section 23 is drained. In its most active stage the heap may need to be cooled with a cooled, recycled biooxidant solution or a cooled maintenance solution, i.e. a nutrient solution.

After the target percentage of oxidized sulfide in section 23 of heap 20 has been reached and the heap has been drained, the heap is then washed for a prolonged period of time as schematically depicted by section 24 of heap 20. After a suitable wash period of e.g. 2 weeks or as determined by residual acidity or iron content target in the wash solution, section 24 is reconstructed by breaking it apart and by means of conveyor belt 3 the ore is reagglomerated with cement and/or lime to make a new heap 25 for leaching it with either cyanide or a thiosulfate solution.

Figure 6 illustrates schematically an embodiment which allows the practice of the invention in a more restricted area, i.e., a "circular" heap 26 is constantly being formed and reformed. Thus the heap expansion zone 32 which represents an empty surface area, is gradually moving around the circle formed by the "circular" heap 26. As new layers of ore 7 are being added at face 30, the agglomerated/inoculated ore of the specific particulates gradually approaches the new face 31 of the freshly inoculated ore 7.

From a correspondingly moving removal front 33, the ore is being taken away to a leach heap such as shown in Figure 5 as 25. Likewise a moving wash front 27 and its corresponding new wash front 28 illustrate the wash section 35 being treated to reduce acidity of the biooxidized ore in the "circular" heap 26.

As shown in Figure 7, a series of individual heaps may be operated for biooxidation. After the biooxidation reactions have been started in heap 8 and have been completed, the heap becomes heap 23a which is allowed to drain. A previously drained heap 23a is washed and is designated as 24a.

Waste water 37 from heap 24a is combined with drain solution 38 from heap 23a and also optionally with a slip stream from heap 8. Although new heap 40 particulates have been previously agglomerated and inoculated, if necessary, supplemental bacteria solution may be introduced in heap 40 which is undergoing biooxidation of sulfides in the ore material.

For the above embodiments, a heap in its biooxidation phase may be operated with a biolixiviant recycle of from 3 to 8 days and about 3 to 8 days of a rest cycle, such as a nutrient or a moisture maintenance cycle. About 4 to 7 days for lixiviant recycle and rest cycles provide suitable periods for keeping a heap operating at a desirable level of activity.

Figure 7 thus illustrates the solution management for the entire biooxidation, drainage and wash sequence. It is evident from Figure 7 that all solution values are being reutilized including the acid, ferric ion and drained bacteria. Such combination of solution utilization provides another advantageous aspect for the present invention. This solution management may be applied also to the embodiments illustrated in Figures 5 and 6.

With respect to the term "agglomeration", it is a method term; and, therefore, it is necessary that it be characterized more precisely in some fashion. Hence, for purposes of this invention it has been replaced with an appropriate description of particulate formation, size, size distribution and particle description in an ore body. These particulates are based on appropriate layering, nucleating and coalescing of the ore and

the like particles to achieve in the formation of the particulates the desired particulate characteristics based on the use of a proper acid resistant agglomeration aid and bacterial inoculation. The results are better porosity, permeability, percolation and liquid throughput. Further proper particulate formation as defined herein includes the minimizing of the effect clay has in the particulate "durability" throughout the biooxidation cycle and thereafter the leaching cycle and, hence, the agglomeration and inoculation, the "sticking" together of particles and the resistance to crushing of the particulate material as prepared in accordance with the invention herein.

Still further, for an easy measure of particulate formation as described herein, it is also defined herein in terms of the amount of agglomerating agent used plus the liquid used to form the desired particulates and expressed on a weight basis and a moisture content range for a newly formed ore heap.

The mean rate of iron solubilization in accordance with the present invention is another characterizing feature for establishing proper particulate formation of the ore material with the agglomerating aid and the biooxidant bacteria material. A threshold iron solubilization rate defines a value which is better than of an unacceptable particulate formed by an inadequate agglomeration. The foregoing indirectly characterized porosity and proper particulate formation.

Another method by which the proper particulate formation is defined is the lag time before a marker element appears in the leaching solution. Such marker elements and conditions have been defined herein with respect to a gold/iron-sulfur matrix system as total soluble iron, soluble ferrous iron, soluble ferric iron, the ratio of ferric to ferrous iron which should be greater than about 4:1 and preferably greater than about 3:1, soluble arsenic, pH, and Eh. Further, the rate of leaching and the leaching solution introduction based on nutrient sufficient and nutrient starved solutions have also been shown. While iron has been used as a marker in the foregoing description, another metal that is solubilized by the biooxidation also is suitable as a marker.

Turning now to the ore preparation prior to particulate formation, the ore is a run-of-the-mine stock or has undergone crushing i.e. either primary or secondary crushing. The ore particles are of a size distribution that has been found to be more appropriate for particulate formation. Appropriately ground ores when used for proper particulate formation are selected so as to obtain the highest rate of biooxidation concomitant with most economic crushing of the particular ore. That is for easy- to-crush ores, the size is less e.g. 1/2 inch (12,7 mm) to minus ten mesh size but for hard to crush ores from 1 (25,4) to 1/4 inches (6,3 mm). Typically an adequate void space is obtained from the above sized particles. Void space may be obtained by a combination of particle sizes of certain distribution, the particle shape and the shape of the formed particulates. Uniformly nearly round particulates with appropriate void space is a desideratum, but it is difficult to achieve this desired particulate and void space configuration for the heap. The reason for such difficulty is that the fracture characteristics of ores are different for different ores. Proper formation of the particulates tends towards rounder, layered particulates by the biooxidant bacteria solution whereupon smaller particles (each of which in turn are individually coated) are further increasing the surface to volume ratio. Hence particulate formation for biooxidation purposes serves the function of increasing surface area but more importantly achieving crush resistant yet individually bacterially treated, increased surface area particulates tolerating a high clay content.

This physical-chemical reactant coaction has resulted in a particulate type that makes bioleaching a practical alternative and makes it a practical method for heretofore considered waste materials of low metal, particularly low gold, and low sulfide content.

Added to the above particulate description is also the fact that biooxidant inoculation readily initiates the biooxidation reaction. That reaction contributes to a rapid direct, indirect and galvanic leaching. Thus, e.g., ferric sulfate produced by the biooxidation reaction accelerates the overall reaction and it thus becomes evident that, e.g., occluded gold in the pyrite matrix is now so much more accessible to a second step leaching, e.g. cyanidation.

Alternatively, where the desired metal value is a component of the matrix material and biooxidation solubilizes that metal value, the biooxidant solution functions as a bioleachant and the desired metal value can be recovered directly from the bioleachant stream. In thus reducing the concentration of solubilized metal value in the bioleachant stream, when that stream is recycled through the heap the solubilization of the desired metal value from the ore material is facilitated because of its lower concentration in the stream.

Inasmuch as ore crushing and grinding constitute the greatest part of the expense in formation of a heap, the process is desirably practiced with the largest ore particle size which may be economically justified as it concerns biooxidation. On an economic time basis, the penetrability of the bacterial solution and subsequent leachant solution and the formation of the particle into particulates (as it is now related to biooxidation) allows larger sized particulates, yet, particle size still has a significant role to play. More importantly, the clay particles which are most prone to migration are readily immobilized on the particulate

surface because the agglomeration aid causes them to form a better particulate, especially with the inoculant solution.

Proper ore crushing and particle size are achieved by means well known in the art such as disclosed e.g. in Perry's "Chemical Engineer's Handbook", 4th Ed., Chapter 8, McGraw-Hill (1973).

5 Appropriate particulate formation, e.g., by agglomeration aids, may be effected with ores having initial moisture content from about 2% to 3% such that the added liquid forms a total moisture content in the ore of about 8% to 12% at maximum. Higher amounts tend to produce unworkable mixtures.

Excess use of the liquid will only be wasteful unless the ore is conjointly mixed with a dry and fine ore and the particulates formed in the combination of the two. Moreover, use of ore "slimes", i.e. fine particles,
10 may now be suitably employed in the particulate formation process.

However, it has been found that it is best that the particulate formation of the ore takes place in such a manner that the inoculation solution-caused build-up of layers or coalescence of particles is achieved in the most efficacious manner such as by the disclosed conveyors shown in Figure 1 and like methods but also employing the useful agglomeration aids, e.g., a polymeric mixture of the type derived herein.

15 Other processes for particulate formation which may be practiced are such as disk type agglomeration devices well known in the art and as further disclosed in literature and handbooks, such as Perry's "Chemical Engineer's Handbook", 4th Ed., Chapter 8-57 et. seq.

An interesting approach to particulate formation is the method disclosed in U.S. Patent No. 4,960,461 which suggests itself as another candidate method having suitability for the present purpose; however, it is
20 noted that before the nip compaction takes place the liquid with its bacterial culture must thoroughly be distributed in the ore material.

For high clay content ores it may also be necessary to establish the requisite amount of agglomeration aid and use a further binding agent, e.g. acid resistant polymers or copolymers for improving the binding, i.e., "sticking", provided for by the bacteria-containing solution are especially desirable. Clay-containing
25 ores are most difficult to bioleach as clay tends to absorb large amounts of water, clogs the solution flow channels and also is easily stripped from the particulates thus forming an impenetrable layer in the heap and causing phenomena such as "perched" water tables in a heap. Ore material containing fine particles is also difficult to bioleach since the fine particles migrate quite easily in the heap with liquid flow through the heap. These fines tend to plug the liquid channels in the heap to the same effect as clays.

30 With ore materials having a clay content greater than about 10 weight percent or a fines content greater than about 30 weight percent -200 mesh or a combined clay content greater than about 5 weight percent and fines content greater than about 25 weight percent -200 mesh, it is desirable to incorporate an agglomeration aid or agent into the particulate formation process as a binding agent. Typically, the amounts added are about 0.05 (0.02) to about 10 lb (4.5 kg) per ton of ore material. The term "fines" as used herein
35 refers to particle material that passes through a 200 mesh sieve, that is, particle material that is minus 200 mesh.

Acid-resistant, microbial biooxidant-compatible, water-soluble vinyl addition polymers comprise agglomeration aids for use in the invention. Such vinyl addition polymers need to be acid-resistant because the microbial biooxidants, such as *T. ferrooxidans*, require an acid environment for survival and iron and sulfur
40 oxidation, i.e., physiological activity. Further, the metabolism of these microorganisms produces acid and tends to lower the pH of their environment. Acid is also useful in the leaching of material from the heap. Hence, microbe-generated acid is preferred for process efficiency. The polymer agglomeration aids need to be microbe-compatible in the sense that these should not be microbiocidal or impair the viability and metabolism of the microorganisms or shift their metabolic pathways detrimentally. The polymeric agglomeration aid desirably is not only compatible with the microbial biooxidant, but it is also unaffected by the
45 biooxidation process engendered by the biooxidant as well. Preferably, the agglomeration aid should not act as a metabolic substrate for the biooxidant nor, even more preferably, should it act as a physical support or attachment for the biooxidant or its colonization. The agglomeration aids need to be water-soluble so that these can be readily applied either in solution or as a dry powder by dusting and then subsequent wetting
50 in particulate formation.

Preferably, the vinyl addition polymer is both acid-resistant and alkali-resistant. Alkali resistance permits the use of alkaline environment lixiviants, such as caustic cyanide or thiosulfate, to be used for metal value recovery without reagglomerating the ore material with a separate alkali-resistant agglomeration aid and then reconstituting the heap. See U.S. Patent Application Serial No. 07/861,563, filed April 1, 1992 the
55 disclosure of which is incorporated here by reference with regard to thiosulfate leaching.

Vinyl addition polymers are those polymers that polymerize upon addition of vinyl or acrylic monomers in solution with a free radical. Such polymers have ionic functional groups. In this regard, see U.S. Patent No. 4,802,914, issued February 7, 1989. Suitable vinyl addition polymers are selected from the homo-

polymers, copolymers, terpolymers or higher polymers of a compound represented by the general formula:
General Formula 1



5 where R is a nitrile, an amide, a carboxyl radical, COOR¹ wherein R¹ is a lower alkyl radical, preferably having from 1 to 4 carbon atoms, and the water soluble salts thereof. In this regard reference should be made to the disclosure of U.S. Patent No. 3,418,237 issued December 24, 1968. Suitable monomers include acrylic acid, methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid, cinnamic acid, beta-styrylacrylic
10 acid, itaconic acid, citraconic acid, maleic acid, fumaric acid, maleic anhydride, dimethylaminoethyl-methacrylate, styrene, ethyl acrylate, methyl acrylate, methylmethacrylate, ethylmethacrylate, acrylamidomethylpropanesulfonic acid, ethyl methacrylate, butyl acrylate, isobutyl acrylate, dodecyl acrylate, 2-ethyloxy acrylate, vinyl acetate, vinyl propionate, vinyl butyrate, alpha-methyl styrene, vinyl toluene, propyl vinyl ether, butyl vinyl ether, isobutyl vinyl ether, methyl vinyl ether, ethyl vinyl ether, vinyl chloride,
15 vinylidene chloride, and the like. In this regard, reference should be made to the disclosures of U.S. Patents Nos. 4,405,728; 4,802,914 and 5,034,139 issued September 20, 1983; February 7, 1989 and July 23, 1991. Preferably, the monomer is acrylamide or acrylic acid or both. It should be understood that the nitrile, amide and R¹ radicals in General Formula 1 may be substituted and that the homopolymer, copolymer, terpolymer or higher polymer may be modified without departing from the spirit of the invention.

20 Preferred polymer candidates are unsubstituted and substituted (1) homopolymers of an acrylamide, (2) homopolymers of an acrylic acid, (3) copolymers, terpolymers and higher polymers of an acrylamide with one or more nonacrylic acid monomers, (4) copolymers, terpolymers and higher polymers of an acrylic acid with one or more nonacrylic acid monomers, (5) cationic and nonionic copolymers of an acrylamide and an acrylic acid or their derivatives as monomers and (6) terpolymers and higher polymers of an acrylamide and
25 an acrylic acid and one or more other monomers. The preferred monomers, acrylamide or acrylic acid or both, may be copolymerized with other monomers such as N-vinyl pyridine, vinyl acetate, styrene, vinyl esters, vinyl halides, vinyl ethers, or unsaturated hydrocarbons such as isobutylene.

By "cationic" polymers are meant polymers synthesized from cationically charged monomers that tend to exhibit a positive charge. By "nonionic" polymers are meant polymers from monomers in which the charges
30 are sufficiently small that the resulting polymers can be considered not to exhibit ionic behavior. In this regard, see U.S. Patent No. 4,751,259, issued June 4, 1988 and U.S. Patent No. 4,898,611, issued February 6, 1990. Suitable cationic monomers are those containing amino or imino groups that produce water-soluble polymers compatible with the selected microbial biooxidants. Such monomers may be selected from N-vinylpyridine and substituted derivatives thereof; alkylamine and N-alkyl substituted derivatives thereof;
35 aminoalkylacrylates and dialkylaminoacrylates, such as aminoethyl acrylate hydrochloride or aminoethyl methacrylate hydrochloride; and N-substituted-(N'-dialkylaminoalkyl) acrylamides and salts thereof. The foregoing may be substituted such as with lower alkyl groups of from 1 to 4 carbon atoms. In addition, other cationic polymers may be obtained through copolymerizing a nitrogen-containing monomer with one or more monoethylenically unsaturated monomers by vinyl polymerization to produce a water-soluble, micro-
40 bial biooxidant-compatible polymer. Suitable monoethylenically unsaturated monomers may be selected from acrylamide, methacrylamide, acrylonitrile, lower alkyl esters of acrylic and methacrylic acids, vinyl methyl ether, N-vinyl oxazolidinone and N-vinyl pyrrolidinone. With regard to cationic monomers see U.S. Patent Nos. 3,259,570 (issued July 5, 1966) and 3,171,805 (issued March 1, 1965). For example, cationic copolymers of acrylamide and acrylic acid and their derivatives as monomers may be copolymers of
45 acrylamide and dimethylaminoethyl methacrylate. In this regard, see U.S. Patent No. 4,898,611, issued February 6, 1990. In addition, nonionic polymers such as polyvinyl alcohol may be considered. In this regard, see U.S. Patent No. 4,013,606 issued March 22, 1977. Nonionic polymers can also be prepared by providing a balanced amount of cationic and anionic groups in the polymer so that while the polymer molecule as a unit is nonionic the cationic and anionic functional groups are available to act cationically or
50 anionically, as the case may be, with respect to a substrate. Hence, the foregoing cationic components can be present in the same polymer molecule with anionic components, such as those derived from acrylic acid or methacrylic acid.

Generally, the polymer agglomeration aid should have a weight average molecular weight from about 10,000 to about 25 million and preferably a medium to high molecular weight, such as a weight average
55 molecular weight from several hundred thousand to several million and preferably greater than about one million.

Preferably, the agglomeration aid may also include a surfactant or demulsifier such as an ethoxylated alkyl phenol, an ethoxylated amine or an ethoxylated fatty alcohol. Preferred surfactants are ethoxylated

alkyl phenols having at least one alkyl group of from 6 to 12 carbon atoms and an average of up to 30 ethoxylate groups per molecule. Ethoxylated octylphenol and ethoxylated nonyl phenol are preferred ethoxylated alkyl phenols.

A desirable anionic polymer is a polyacrylamide available as NALCO 8877 flocculent from NALCO Chemical Company. NALCO 8877 is a moderately anionic, high molecular weight, single component liquid flocculent that can be applied at an application rate generally from about 0.05 (0,02) to about 5 pounds (2,26 kg) of polyacrylamide per ton of ore material and preferably from about 0.1 (0,04) to about 2.5 pounds (1,13 kg) per ton. This material provides high agglomeration performance over a wide range of heap pH conditions without breakdown of the particulates and the migration of clays or fines. The material is particularly suited to the acidic and oxidative conditions that exist during biooxidation. Nor does it have a deleterious effect on the performance of the microbial biooxidant. In addition, the surfactant used with this acrylamide - ethoxylated nonylphenol - is also compatible with the biooxidant. At a concentration of one weight percent in deionized water it has a pH of 7.

A preferred nonionic polymer is a polyacrylamide available as NALCO 8871 flocculent from NALCO Chemical Company. NALCO 8871 is a nonionic, high molecular weight, single component liquid flocculent that can be applied as an agglomeration aid at an application rate generally from about 0.05 (0,02) to about 5 pounds (2,26 kg) of polyacrylamide ore material and, preferably from about 0.1 (0,04) about 2.5 pounds (1,13 kg) per ton. This material has no charge in solution and is believed to provide high agglomeration performance over a wide range of heap pH conditions. The material and its associated surfactant, ethoxylated nonylphenol, are believed to provide biocompatibility with microbial biooxidants.

Each of the foregoing NALCO materials readily dissolves in water making it easy to use in the formation of particulates using binding agent solutions. Owing to their excellent settling, clarification, thickening, and dewatering properties in processing mineral slurries, they are easily used in agglomerating ore particles and clays and/or fines into particulates. As single component polymeric flocculents, they need no activator, thereby making their use simpler and less costly.

A preferred agglomeration aid comprises NALCO 8877 flocculant at one weight percent of a polyacrylamide (available as from NALCO Chemical Company); 1-5 weight percent of ethoxylated nonylphenol or ethoxylated octylphenol and 20-40% weight percent of hydrotreated light distillate, the remainder being sodium chloride and water. An alternative agglomeration aid available as EXTRACT-ORE 9760 agglomeration aid from Nalco Chemical Company comprises one weight percent of acrylic polymer and esterified olefinic polymer, 1-5 weight percent ethoxylated octyl phenol, 20-40 weight percent hydrotreated light distillate, the remainder being water.

The agglomeration aid should be applied generally at a rate of about 0.05 (0,02) to about 10 pounds (4,53 kg) of polymer per ton of ore material, preferably from about 0.1 to about 5 pounds per ton and optimally from about 0.1 (0,04) to about 2.5 pounds (1,13 kg) per ton. The agglomeration aid can be applied as a dry powder, a stream of solution, a spray of liquid droplets or a foam.

Inasmuch the various aforementioned monomers can be present in various percentages in the polymer and their interrelationship to the various polymers, copolymers, terpolymers and higher polymers in terms of mole percentages present an excessive number variables, the easiest way to provide for an objective standard and for enablement is to compare the agglomeration aids of the invention, including acid-resistant cationic and nonionic agglomeration aids, to the herein-disclosed specific agglomeration aids, such as the polyacrylamide available as NALCO 8877 from NALCO Chemical Company. The thus-established objective standard provides a scale of performance of 1 to 5 (with a low value describing a worse performance) and with respect to the herein-disclosed standard (NALCO 8877 polyacrylamide) which defines an acceptable i.e. 2.5 value and thus affords a comparison for the agglomerative properties of the specific agglomeration aid being tested. This rating system permits one to evaluate the suitability of an agglomeration aid for use in the invention with respect to agglomerative properties.

Similarly, acid-resistance of an agglomeration aid of the invention can be measured on an objective scale of 1 to 5 by comparison with the acid resistance of a herein-disclosed standard, such as NALCO 8877 polyacrylamide for which a value of 2.5 is given, in maintaining sufficient particulate integrity over a period of time such as at least 200 days in an acid environment of pH 1.3 to 2 and, preferably 1.8, in order to permit caustic cyanidation (with a value of 1 describing the worst performance with respect to the standard.) Thus, a means is provided to permit one to evaluate the performance of an agglomeration aid for use in the invention with respect to acid resistance. Since the properties of the particulates vary over the long term and, further, due to the inherent long duration of biooxidation, the valuation based on the aforesaid objective standards of agglomerative ability and acid resistance are a reasonable approach to the need for a constructive reduction to practice of the invention. Concurrently with acid resistance, biooxidation resistance is also measured in the same manner employing the same standard (NALCO 8877) as above based on the

same scale. There should be a balance of the three properties of agglomerativeness, acid-resistance and biooxidation resistance in a sequentially applied regime with the values, on average, of each falling preferably from about 2 to about 5 and more desirably from about 2.5 to about 5 such that if a higher acceptable value is achieved for agglomerativeness, a lesser value would be acceptable for the remaining properties. The average of the three properties should be about 2.0 and above; preferably 2.5.

In the invention the foregoing agglomeration aids are utilized in the formation of particulates from particles comprising ore material and clays and/or fines material in cooperation with an inoculate comprising bacteria capable of at least partially biooxidizing the sulfur content and, optionally, an acid treatment. The particles are preferably treated with the agglomeration aid and inoculate concurrently with the formation of the particulates or sequentially in which the particulates are treated with agglomeration aid and then formed into particulates in the presence of the inoculate. Generally, the particles can be treated with the agglomeration aid prior to particulate formation or concurrently with formation. Also, the ore particles can be treated with inoculate before, during or after particulate formation. The particles may be pretreated with acid before formation of particulates or after the particulates may be formed in the presence of acid.

Typical particulate formation is by spraying of the liquid on the ore. Dipping into a liquid bath an ore conveyor belt and other means such as use of screw extruders and the like may be employed. It is important, however, that the moisture content and the particulate formation be such that the distribution of particles and sufficient surface area are achieved with the inoculation which provides for the fast reaction times, i.e. induction and oxidation of the sulfide reactants at economically acceptable rates.

For example, the present invention contemplates the proper particulate formation of a distribution of fine and coarse ore material particles with the concomitant proper and far better and more dense distribution of the biooxidant bacteria mass as shown in Figure 2.

In accordance with the invention the following bacteria have been found to be useful. These bacteria are either available from American Type Culture or like culture collections or have been made available thereto and/or will be made available to the public before the issuance of this disclosure as a patent.

- Group A. Thiobacillus ferrooxidans;
Thiobacillus thiooxidans;
Thiobacillus organoparus;
Thiobacillus acidophilus;
- Group B. Leptospirillum ferrooxidans;
- Group C. Sulfobacillus thermosulfidooxidans;
- Group D. Sulfobolus acidocaldarius, Sulfobolus BC; Sulfobolus solfataricus and Acidianus brierleyi and the like.

The above bacteria are further classified as either mesophiles (Groups A and B) i.e. the microorganism is capable of growth at mid-range temperatures (e.g. about 30° C) and facultative thermophiles (Group C) (e.g. about 50° to 55° C); or obligate thermophiles (Group D) which are microorganisms which can only grow at high (thermophilic) temperatures (e.g. greater than about 50° C).

It is also desirable when applying the present invention to ore materials in which the desired metal value(s) and/or the matrix material comprises an inorganic metallosulfur compound in which the metal moiety is other than iron that bacteria may be utilized that also oxidize the selected metal.

For the above ore particulates to be usefully biooxidized, typically ores should have a certain mineralogy. The candidate ores should not contain more than 1% to 10% of calcite, dolomite, or other carbonate minerals and should have at least 0.2% sulfide present (all percentages and parts herein are by weight, unless expressed otherwise). The calcite carbonate makes the ores acid consuming and very refractory to treatment. These type ores should also have high sulfide content to generate the acid required for carbonate neutralization and sulfuric acid may have to be added to control the pH in a range suitable for biooxidation.

Appropriate bacterial biomass production may be practiced, e.g. as disclosed in U.S. Application Serial No. 07/695,945 filed May 6, 1991, entitled "High Yield Method for Growing Thiobacillus ferrooxidans on Formate".

In accordance with the above description, a solution containing one or more of the above described bacteria in a biomass concentration from 10^5 to 10^9 bacteria per milliliter of solution is used for the formation of the ore particulates from particles in a manner such as to cover the particles with an appropriate layer of bacteria and thereafter, in particulate formation with fines adhering to a nucleus of the material. The build-up of subsequent small particles and particulate materials and the formation of these in a mass having a surface to volume ratio of at least 100 square centimeters per 100 cubic centimeters of ore provides a threshold measure.

Although longer leach times (slower rates) may be tolerated and the present invention contemplates

such low leaching rates, the desirable, preferred method requires that at least an induction period of 5 to 20 days for the same amount of an indicator or marker should be displayed by the ore when treated to obtain a proper particulate formation.

It is to be noted that for Group A. and B. bacteria the useful temperatures should not exceed 35 °C; for Group C. bacteria these temperatures should not exceed 55 °C; and for Group D. bacteria the temperature should not exceed 80 °C. Consequently, based on a temperature profile in a waste ore heap when oxidation of sulfides is in full swing and sulfide oxidation exotherm is highest, the heap may be bathed with cooled leachant or constructed with cooling (and/or heating) provisions. Further, the heap may be constructed with the appropriate bacteria to meet the temperature limits for such an ore, i.e. for high sulfide content ores. As it is well known and based on sulfide oxidation rates and concentrations, the temperatures in a leached heap are not uniform and the bacteria are often not able to survive if the temperature is not appropriately controlled or if the proper bacteria are not used. Therefore, the proper construction of a waste ore heap with the particulates formed with the proper thermophilic bacteria solution anticipates the encountered temperature in the ore body and thus is an advantage of the present invention.

Subsequent inoculation of the ore with additional and different bacteria may further accelerate the rate of reaction and is within the contemplation of the combination process disclosed herein. This inoculant use after heap formation further enhances the attractiveness of this process and makes it especially desirable when treating multi-metal containing ores having metals with biocidal properties. For example arsenic resistant strains may be used initially. Arsenopyrites are preferentially (time-wise) dissolved during biooxidation. However, leaching of arsenopyrites produces free or elemental sulfur. Hence, *Thiobacillus thiooxidans* may be used to remove the inhibitory effect of free or elemental sulfur. Also, high cyanide consumption occurs if free or elemental sulfur is present.

As disclosed above, the sulfide oxidation takes place at a pH of less than 2.5 and the operable range seems to be from about a pH 1.3 to about pH 2.0. Lower pH requires special bacteria such as *Leptospirillum ferrooxidans*. For the induction of the reactions, acid consumable components in the ore (which are well known in the art), should be taken into account. Acid consumption would retard or arrest the reaction by withdrawing sulfuric acid present.

Although the bacterial content for an ore material may be estimated such as by counting, by microscopy or end-point dilution (e.g., the Most-Probable-Number method), it is best that the progress of the reaction be monitored by the solubilization rate of arsenic or iron in the pyrites or the oxidation rate of the sulfides which may be calculated therefrom. Such monitoring is usefully demonstrated by reference to Figure 4 from the curves shown in that figure. Other monitoring may be such as by measuring pH, determining titratable acidity, decrease of ferrous iron concentration, oxygen uptake, carbon dioxide uptake etc., etc.

While ultimately all tests for biooxidation efficiency must be based on the results obtained from data gathered in operating a heap, for relatively accurate comparisons, column test data are acceptable such as for an ore material biooxidized in a properly sized column. If it were not so, data gathering would be not only prohibitively expensive but also of an enormously long duration.

In order to aid the solubilization of metals, ferric sulfate may also be added to the reaction solution. An initial ferric sulfate component may be provided with the bacterial liquid used so that the reaction and the redox potential is initially established and immediately raised.

In the event acid pretreatment of ore is employed, the pretreatment may be interrupted before final particulate formation takes place. However, it is advantageous that the acid pretreatment and the particulate formation takes place at about the same time in a continuous sequence because of the high costs associated with reconstituting or rehandling such vast amounts of ore material. The costs associated with material rehandling may render the process economically unattractive.

After the ore particulates have been laid down on a suitable impervious base (and including a coarse drainage aiding layer of material) in a thickness from about 5 feet to about 300 feet, the leaching and/or nutrient supplementation is allowed to proceed as needed. A typical leach solution is of the following composition: from about 10 to 30 grams/liter total soluble iron (predominantly in the ferric form), from about 0.1 to 10 grams/liter arsenic as arsenate, from about 30 to 100 grams/liter sulfate. The heap is sprinkled or kept wet by drip irrigation such as with the leachant or with a nutrient solution. The last is comprised from about .4 to 30 grams per liter of Fe^{3+} ; ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ from about .4 grams per liter initially, to about .1 gram per liter during the course of the operation. Additionally, about 40 parts per million (ppm) of phosphat is also added as th nutrient. Nutrient addition is monitored during the course of leaching and is changed, supplemented or augmented based on the selected performance indicators observed during the monitoring. When the heap is irrigated with either of the leachant or nutrient solution, oxygen concentration in either solution should be at least between .5 and 2 mg O_2 /liter of solution.

The desired pH value is being maintained with sulfuric acid being added in order to work the heap with the solution being in the above indicated pH range of 1.6 to about 2.0. Because there is a certain amount of evaporation, the heap must also be maintained at a certain equilibrium moisture content found necessary for the location; such additions are provided during the course of reaction.

Because the heap is also non-repairable in a sense that rehandling of the materials is expensive, the previously described particulate formation and treatment conditions the heap in such a manner as to make for a very efficient biooxidation reactions when compared to the prior art typical tank, or vat methods carried out in slurry form involving liquid handling and liquid inoculation of the ore materials treated by biooxidation solutions. Moreover, the present invention allows treatment of ores of low sulfide content.

Likewise, the present invention differentiates from the typical biooxidation reactions in which the biooxidant solution is sprinkled or dripped on the heaps to develop the bacteria colonies over the period of time. Such prior art distribution is also very inefficient time-wise in that the dispersal and distribution is non-uniform. In such heaps, the bacteria tends to be concentrated only in the top one to two feet. Equilibrium conditions in such heaps are difficult to maintain and the reaction proceeds at a rate found to be incapable of duplicating the results which have been found herein. Bacterial survivability thus depends on only the top layers of an ore heap and the heap has large dead regions. For this reason, prior art bioleaching attempts have often been confined to forming of shallow heaps.

After reasonable equilibrium conditions are achieved following the induction period (the lag time), the progress of the biooxidation reaction, after maintenance cycle bioleachant additions, is monitored by appropriate markers which provide the direct or indirect indications for the oxidation rate of the sulfides and termination conditions. For example, arsenic and iron are being used as marker elements which define the oxidation of the sulfides based on the amount of arsenopyrite and pyrite sulfides being present. Inasmuch as the biooxidation reaction rate is controlled by the attachment of the bacteria to the ore, i.e. substrate, the present method provides for especially advantageous mechanism to overcome this rate limiting step when practicing the prior art conventional heap bioleaching process. Other reaction conditions which illustrate the diffusion efficiency of the biooxidant as well as reaction rate for the process herein are shown by the amount of other materials found in the solution as well as the ultimate extractability of the desired metal, such as gold. Other marker species which may be used are those typically found in conjunction with the desired metal, such as precious metals, for that particular ore and may be monitored for that purpose as befits the ore of the particular mineralogy.

With respect to the temperature at which the heap seems to operate optimally, it is based on the ambient conditions encountered in the area in which the heap has been formed. The interior of the heap resists exterior ambient temperature changes and varies very little except for the exothermic sulfide oxidation reaction. These exothermic temperature associated problems have been discussed previously.

The bioleachate is recycled at a rate from about 0.005 gallon (0.002 liter) per minute per square foot (dm^2) of top surface area for the ore body. A suitable rate varies from about 0.003 gal/min/ ft^2 (0.001 l/mn/ dm^2) to 0.01 gal/min/ ft^2 (0.004 l/mn/ dm^2). A preferred range for the rate is from 0.004 (0.0019) to 0.006 gal/min/ ft^2 (0.0029 l/mn/ dm^2). Dispersal of leachant may be achieved by well known means illustrated in the art for typical heap leaching processes but drip irrigation is preferred. In addition to solution application using drip irrigation, "wobblers" or spraying the solution may be advantageous. Spraying the solution on the heap can increase oxygen content in the solution, and this method can also be used to control excess solution through increased evaporation.

From experience, the sulfide oxidation achieved is about 50% to 60% on a time scale based on economic considerations. It is desirable, although not mandatory, to have as high degree of sulfide oxidation as possible. It is also desirable for any elemental sulfur content to be oxidized, particularly if it participates in the occlusion of the desired metal value(s). Inasmuch as the iron oxidation (or other selected metal oxidation) correlates to sulfide oxidation, the reaction can be reasonably well measured thereby. It has been found that at the lower end of the range about 50% to 60% of the sulfur remains in the ore and can still be tolerated. However, if the reaction rate is acceptable, higher sulfur oxidation is contemplated and may be of benefit in subsequent metal value(s) recovery, such as by cyanidation, as will be further discussed therein.

During the bioleachate recycle a slip stream may be provided for the removal of Fe^{3+} ; typically about 30 grams per liter of Fe^{3+} in the heap effluent is considered to be fairly well the upper limit. Thereafter, iron may start to affect the reaction rate because of inhibitory effects and if arsenic ions are present, these contribute to the inhibitory effect. As arsenic is a biocide, it is best that the amount of arsenic is not allowed to exceed about 14 grams per liter. The arsenopyrites are preferentially attacked by the biooxidant. If the bacteria are appropriately adapted and the bacteria had a chance to adapt themselves, which is a condition in nature in the high arsenic ore mines, then the reaction may proceed initially and thereafter with fairly large amounts of arsenic present. Hence, biooxidation contributes to the removal of excess unwanted

arsenic. Arsenic may be removed by coprecipitation with iron under suitable conditions. Typically, arsenic as arsenate (As^{5+}), and iron, as the ferric species (Fe^{3+}), will coprecipitate when the solution ratio of Fe:As exceeds 4:1 and the solution pH exceeds 3. Lime is used to raise the solution pH to facilitate the coprecipitation reaction. The resulting ferriarsenate is reportedly a very stable compound with little tendency to dissociate. Also, the presence of ferriarsenate and iron arsenates in general causes high cyanide consumption.

Similarly in systems in which another metal is bioleached, a slip stream may be provided for the removal of that metal and its recovery. Further, the entire bioleached stream may be treated to recover that metal. In each of these instances the recovery of the desired metal is made directly from the bioleachate stream and metal recovery is made a part of the biooxidation/bioleaching stage and a separate recovery stage is not needed. Suitable techniques for recovery of desired metal values from bioleachate solution before recycle are:

1. precipitation;
2. solvent extraction and/or
3. ion exchange

After the biooxidation reaction has come to an economically defined end point, the heap may be then be drained and washed out by repeated flushing with water. Generally about two weeks of washing is sufficient. Washout cycles and times are based on an appropriate marker element such as iron and the pH of the wash effluent. A target amount is about 500 ppm of Fe in the wash effluent.

Inasmuch as the solution inventory and solution handling is a sizeable part of the expense in heap leaching, it is also important that the solution management is properly carried out as previously discussed in conjunction with Figure 7. One aspect of the biooxidation-heap pretreatment process related to solution management is the use of the biooxidation recycle-solution as inoculant for particulate formation - with the recycle solution as an inoculant for new ore being modified as needed. The solution drained from the heap, prior to washing, will be acidic and contain bacteria and ferric iron. This solution can then be advantageously used for particulate formation with the recycle solution, i.e. inoculant solution of ore coming into the treatment process. In addition, the wash water will also contain the bacteria and ferric iron at an acidic pH and could be used if appropriately augmented, e.g. by leachant from the biooxidation stage for particulate formation and bacteria inoculation. This is a way to manage the solutions in the process and to decrease the need for waste water treatment until such time that inoculation is no longer required. For the present method, the solution management is vastly improved because of the fast reaction initiation rate and the faster leaching reaction. Consequently, less solution volume needs to be handled in order to achieve the equivalent amount of recovery when compared to a heap which has been traditionally prepared and bioleached and cyanide leached.

In addition to the leachant recycle and reuse, air and possibly carbon dioxide circulation may also be necessary which may be achieved by sparging into the leachant solution appropriate amount of air or oxygen or by directly injecting into the heap the appropriate amount of the gases. At higher oxygen amounts, e.g. at much greater than saturation level of about 8 mg/liter of solution oxygen also is inhibitory of the reaction. Typically, oxygen should not exceed 25 to 50 ppm of leachant.

As previously mentioned besides the initial agglomerate biooxidation bacteria solution, a consortium inoculant solution may also be practiced as disclosed in a companion application. This disclosure is incorporated by reference and is found in Serial No. 07/750,444, filed on August 20, 1991, entitled "Microbial Consortium Treatment of Refractory Precious Metals Ores".

In practicing the process, one must guard against contamination of the system by extreme biocides, e.g. a biocide type of surfactant and anti-scaling compounds.

With respect to metal recovery by a separate leaching or lixiviation stage, after the post treatment and washing of the heap and after the heap has reached the desired pH range such as for thiourea extraction which may be practiced within a pH range from 1.5 to 2.0, the thiourea lixiviant is then introduced into the heap and the heap is being worked-up by the thiourea solution. Typically, about 0.1 gr/liter to 10 gr/liter of thiourea is used. A preferred range is from about 0.2 to 5 gr/liter in the lixiviant. Thiourea solutions may contain, as reducing agent, sulfite to improve thiourea leaching efficiency. Other agents which may be added are sulfuric acid for pH control and citric acid for thiourea stabilization. An appropriate thiourea leaching is described in U.S. Patent No. 4,902,345, granted on February 20, 1990 for "Treatment of Refractory Carbonaceous and Sulfidic Ores or Concentrates for Precious Metal Recovery"; and Brierley et al, "Enhanced Recovery of Gold from Refractory Sulfidic-Carbonaceous Ores Using Bacterial Pretreatment and Thiourea Extraction", Gold '90 Symposium Proceedings, AIME, March 1990. The disclosure of these are incorporated by reference herein.

Thiourea is not as attractive a reagent as cyanide because the cost of the lixiviant material. Typically for

thiourea leaching, the recovery of gold is not as high when compared to cyanide. Although the cost of reconstituting a heap for cyanide leaching may outweigh the disadvantages for thiourea leaching, it has been found that thiourea offers a number of advantages based on environmental considerations.

In a similar manner, a thiosulfate, e.g. ammonium thiosulfate or sodium thiosulfate, may also be used. Typically, an ammonium thiosulfate leachant operates in a pH range from about 8 to 10 and, preferably at a pH of at least about 9; and, therefore, the bioleached ore requires some neutralization. If direct neutralization is attempted such neutralization becomes extremely costly as well as likely to cause plugging of the heap by iron hydroxide formation. Hence, neutralization may be attempted by other means such as spoiling the heap and adding either cement or lime, or the mixture of the two to bring the heap within the pH range suitable for thiosulfate extraction. Thiosulfate solubilized gold is recovered by cementation or sulfide precipitation. Typically the cost for thiosulfate leaching is less than for thiourea but the thiosulfate leaching disadvantages are the cost of heap reconstruction and neutralization. These competing costs must then be balanced out in order to select the option which provides the advantages.

Cyanidation of the ore in a heap is also very attractive. Consequently, one of the advantages of the present process is the strong particulate which allows washing of the heap and the ability not to need to reconstitute the heap. The heap may also be properly reconstituted. According to the present invention, reconstituting of the heap is achieved with additional lime, Portland cement, caustic soda, cement dust or mixtures of these by thoroughly mixing the ore with the neutralizing agent and then agglomerating the ore. Because of the fairly high lime consumption, the neutralization reaction must proceed in a manner such as to improve the contact of lime with the still fairly acidic ore material. The ore is acidic despite its washing, and is in a pH range from 1.5 to 5. Neutralization is practicable with the acid- and alkali-resistant agglomeration aid and may also be improved by breaking up the biooxidized heap and, by means of conveyor, or like devices reconstituting the heap. Advantageously it has been found that neutralization and reconstitution by appropriate particulate formation has certain advantages derived from the original biooxidation attributed to it by biooxidation and initial particulate formation (which has unexpectedly benefitted the subsequent extraction of gold by the cyanide). Such step-wise treatment and particulate formation has provided appropriate porosity, good percolation, good access by the cyanide ion, and the proper distribution of the lixiviant solution. It has been found that the void space and surface to volume ratios are about the same as for biooxidation but the lower limits are based on the values given above for biooxidation. The reconstituted heap is also aged or cured for about 1 to 2 days for it to function in a desirable manner.

After the heap has been treated with the cyanide solution for an appropriate length of time, typically based on a defined final limit amount of gold in the lixiviant solution, the heap may then be rendered dormant by washing or by the introduction of an appropriate fungi or other microorganisms which destroy the residual cyanide present in the heap. Cyanide degrading fungi are disclosed, e.g. in U.S. Patent No. 4,402,831, granted September 6, 1983.

In conjunction with cyanide treatment, the lixiviant may also have added thereto appropriate surfactants, oxygen or ozone or mixtures of these such as disclosed in the prior art. As for biooxidation, the same hold true for cyanidation -- leach and rest cycles of the same order of length of time may be used to improve gold extraction. Similarly if a heap displays some disadvantageous clogging it can be opened up such as disclosed in U.S. Patent No. 3,819,797.

Based on the above cyanide extraction, it is well known in the art to employ lixiviant solutions such as based on sodium cyanide or potassium cyanide. Recovery of gold is from about 35% to about 80% based on an analysis which includes the determination of gold in leach solution by atomic adsorption spectroscopy, fire assay of the leached ore residue and fire assay of the carbon used to recover the gold. In those instances where the desired metal value(s) are present as compound(s) dispersed within or occluded in a biooxidant matrix material and those compound(s) are not themselves biooxidized, the biooxidation has rendered those desired metal value(s) more accessible to recovery (having been freed of the matrix material to at least some degree.) The now-accessible metal value compounds are now amenable to further processing and metal value(s) recovery suitable for the compounds in which they are present.

In the examples to follow various aspects of the invention are further amplified and such amplifications are intended to be illustrations, but not limitations, of the invention disclosed herein.

EXAMPLE 1

A culture of *Thiobacillus f. roxidans*, or a similar microorganism capable of iron oxidation and growth in acidic conditions, is grown in an acidic nutrient solution. A typical nutrient acid solution contains the following: 400 mg/l ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$; 40 mg/l potassium phosphate dibasic (K_2HPO_4) ; 400 mg/l magnesium sulfate heptahydrate $(\text{MgSO}_4 \cdot 7\text{H}_2\text{O})$; 33.3 g/l ferrous sulfate heptahydrate $(\text{FeSO}_4 \cdot 7\text{H}_2\text{O})$,

with a pH of 1.6 to 2.0, obtained by adjustment with sulfuric acid (H_2SO_4). The microorganism culture is grown for a period of three to ten days with aeration at a temperature of 20° to 35°C in an amount sufficient to provide the solution required for particulate formation. The microbe-culture solution is applied to the ore to facilitate the previously described particulate formation.

EXAMPLE 2

Laboratory experimentation for evaluation of microbial pretreatment of refractory gold ore samples utilized the *T. ferrooxidans* culture medium (EXAMPLE 1) for particulate formation of the ore samples. Following this particulate formation, the ore was biooxidized in columns. Table 1 lists the parameters of the particulate formation/inoculation procedure.

Table 1

Particulate Formation of ore samples for biooxidation Pretreatment

Table 1

| Particulate Formation of ore samples for biooxidation Pretreatment | | | | |
|--|---|-----------|------------|--|
| Ore Sample | Particulate Mean Size (inch = 25,4 mm) | Amount kg | Moisture % | Culture Medium Agglomeration liters |
| Sulfidic leach grade | - 1/2" | 45.25 | 7.4 | 6.36 |
| Sulfidic mill grade | - 1/2" | 45.35 | 7.4 | 6.367 |
| Sulfidic-carbonaceous leach grade | - 1/2" | 48.65 | 7.0 | 6.367 |
| Sulfidic-carbonaceous mill grade | - 1/2" | 46.15 | 73 | 6.363 |

The acidic particulate formation solution, containing the *T. ferrooxidans* and iron (7 to 8 g total Fe/l), was used at pH 2 to 3. The solution was added at about 0.08 l/kg of ore. The effect of the solution was to form the particulates from the fine particles of ore preventing plugging of the column and facilitating even solution flow.

EXAMPLE 3

Two 500 ton samples (A and B) of crushed ore (nominal size minus 3/4 inch (19mm) were each used for forming the particulates using the culture medium (EXAMPLE 1) and *T. ferrooxidans*. About 5100 gallons (23 185 liters) of culture medium were used for the particulate formation procedure. Following the particulate formation, the ore samples were placed on asphalt pads for pretreatment by biooxidation to enhance gold recovery.

Ore A was substantially a gold-bearing quartz ore containing sulfur in the sulfide and sulfate form. The ore contained by weight 1% iron oxides, 4% jarosite, 10% alunite, 4% kaolinite, 4% sericite, less than 1% pyrite and the balance substantially quartz (about 73% or more). The gold content by fire assay came to 0.051 oz. per ton (1,445 g/t) of ore. The cyanide assay for gold was 0.012 oz per ton (0,340 g/t) of ore, thus indicating that a substantial portion of the gold was occluded within the ore and not free.

The total sulfur content of ore A was about 1.42% of which sulfate sulfur was about 1.22% and sulfide sulfur about 0.31%. The total carbon content was 0.16% which was acid insoluble. The remaining ingredients included 0.666% As and about 2.19% Fe.

Ore B comprised by weight about 1% iron oxides, 3% barite, 3% jarosite, 12% alunite, 6% montmorillonite, 4% sericite, 2% pyrite and the balance substantially quartz (over about 65%). The amount of gold by fire assay was 0.065 oz per ton (1,842 g/t) of ore. Cyanide assay did not show the presence of free gold, thus, indicating that substantially all of the gold was occluded in the ore and not freely available. The analysis also indicated that total sulfur was 2.31%, the sulfate sulfur being about 1.16% and sulfide sulfur about 1.15%. The total carbon content was about 1.27% of which 1.21% was acid insoluble. The ore also contained 0.035% As and a total content of 2.04% Fe.

EXAMPLE 4

The particulate formation from the ore particles (described in EXAMPLE 3) was accomplished by adding the bacterial culture to the ore on a conveyor belt as shown in Figure 1. The culture solution was added at a rate of 16 (72,7) to 20 gallons (90,9 liters)/1.67 tons of ore/minute. Two conveyor-belts plus a conveyor-stacker were used to provide transfer points to facilitate the mixing of the ore with the culture solution.

Inoculation

Effective bioleaching or biooxidation pretreatment requires the presence of an active bacterial population such as the *Thiobacillus ferrooxidans*. Recently mined ore generally does not contain a sufficiently large population of the bioleaching bacteria. In order to initiate rapid activity of the bacteria, and the treatment of the ore, it is necessary to inoculate the ore with the bacteria, particularly for a heap leach process containing a very large proportion of solids to leach solution.

It is preferred to inoculate the ore with microbes such as *Thiobacillus ferrooxidans* during the particle formation procedure. This has the advantage of distributing the bacteria on the ore particles and layering the particulates when these are placed in a biooxidation treatment heap. The inoculation process accelerates the initiation of active biooxidation.

EXAMPLE 5

Samples of sulfidic-carbonaceous gold ore (ore B) were used for forming particulates while inoculated (EXAMPLE 2) for column-test evaluation of biooxidation for enhanced gold recovery. One series of columns were used with formed particulates employing sulfuric acid and the microbes added after the ore was loaded in the column. A second series of columns were concurrently inoculated with *T. ferrooxidans* during the particulate formation procedure. The results (Table 2) indicate that concurrent particulate formation with an inoculation solution of bacteria of the ore increases the initial rate of biooxidation as indicated by iron solubilization.

Table 2

| Inoculation and Particulate Formation to Facilitate the Biooxidation Process | | |
|--|---------------------------------------|---|
| Inoculation | Biooxidation Time-Days (in series) | Biooxidation Rate % Fe Solubilized/Day |
| Microbes added to columns | 30 | 0.24 |
| | 30 | 0.28 |
| | 32 | 0.16 |
| | 30 | 0.30 |
| Particulates formed by use of inoculation solution | 29 | 0.33 |
| | 35 | 0.51 |
| | 33 | 0.41 |
| | 33 | 0.51 |
| | 33 | 0.42 |

The mean rate of iron solubilization from the ore which was treated with acid and then inoculated with the *T. ferrooxidans* was 0.24% Fe solubilized/day. The combined particulate formation with an inoculation solution resulted in an average of 0.44% Fe solubilized/day, an apparent increase of biooxidation rate of 83%. When the inoculation solution is used for particulate formation it also advantageously decreases the lag time, the time required for development of the critical bacterial population size for biooxidation of the ore as seen from the above data for iron solubilization after 30 days and 29 days respectively.

EXAMPLE 6

An experimental biooxidation test heap, containing a refractory sulfidic-carbonaceous gold ore (ore B), was set up for particle formation employing the process as described in EXAMPLES 3 and 4. The

circulating leach solution draining from the heap was monitored for pH, Eh and total soluble iron as indicators of the activity of the *T. ferrooxidans*. The data (Table 3) indicate the presence of an active bacterial population and biooxidation.

Table 3

| Biooxidation of Inoculated Refractory Gold Ore According to the Invention | | | |
|---|------|---------|------------------------|
| Biooxidation Time in Days | pH | Eh + mv | Total Soluble Iron g/l |
| 1 | 2.02 | - | 1.85 |
| 7 | 2.26 | 641 | 3.63 |
| 14 | 1.90 | 617 | 11.44 |
| 23 | 1.77 | 635 | 19.65 |
| 30 | 1.63 | 662 | 21.80 |
| 37 | 1.77 | 667 | 26.55 |
| 44 | 1.70 | 689 | 27.48 |
| 51 | 1.71 | 707 | 27.67 |
| 58 | 1.96 | 718 | 28.41 |
| 65 | 1.87 | 717 | 35.03 |

Eh or redox potential is defined as follows: Eh, or oxidation-reduction potential is a measure of a systems tendency to be oxidizing or reducing. The oxidation-reduction potential is measured electrically in reference to a standard substance, hydrogen (H_2). A system with a high positive Eh, such as the biooxidation solution, indicates that the solution will have oxidizing activity, in this case the oxidizing activity is due to the presence of ferric iron and the absence of ferrous iron (a reducing agent). The increased numbers indicate an increase in ionic concentration, e.g. of Fe^{3+} in the solution.

The particulate formation of added *T. ferrooxidans* was of a concentration of about 10^5 microbes/gram of ore particulates. Following a one-month period of biooxidation, the bacterial population had increased to 10^7 microbes/gram of particulates. Visual inspection of the test heap indicated formation of a stable collection of particulates from the ore particles. The leaching solution, applied at a rate of 0.005 gal/min/ft² (0.002 l/mn/dm², percolated rapidly through the test heap without any apparent ponding.

The leaching solution comprised initially of water plus nutrients acidified with sulfuric acid to about pH 2. Subsequently, only fresh water was used to make up evaporative loss.

An advantage of the invention is that the particulate formation process is effective on ore processed through primary and secondary crushing.

Table 4

| Screen Analysis of Sulfidic-Carbonaceous Ore Used in Biooxidation | |
|---|-----------------------------|
| Size Fraction, inches (mm) | Weight Percent Distribution |
| + 1.50 + 38,1 | 17.70 |
| -38,1 -150 + 1.00 + 25,4 | 28.68 |
| -25,4 -1.00 + 0.75 + 19,05 | 11.57 |
| -19,05 -0.75 + 0.50 + 12,7 | 10.11 |
| -12,7 -0.50 + 0.25 + 6,35 | 12.13 |
| -6,35 -0.25 + 0.08 + 2,03 | 11.25 |
| -0.08 -2,03 | 8.56 |
| TOTAL | 100.00 |

As a preferred embodiment, the ore may be -1/2 inch (-12,7 mm) with at least about 50% of the ore -1/4 inch (-6,35 mm) and at least about 10% -10 mesh (U.S. Standard Screen).

Another preferred embodiment is to wash the particulates following biooxidation of the ore, disassemble

the heap, and reconstitute the disassembled particulates with cement (e.g. Portland Cement) or cement plus lime as the binder to provide reconstituted particulates with a pH in the range of about 8 to 11, preferably 9 to 11 for subsequent cyanide leaching.

The amount of cement may comprise about 10 lbs. per ton (4,53 kg per ton) of ore, or about 0.5% of the total weight of the ore. The amount of cement or other binder employed may range from about 3 (1,36) to 15 lbs. per ton (6,80 kg per ton) of ore.

Where the biooxidized ore ready for leaching is acidic, a thiourea solution may be used to recover the precious metals. A typical thiourea solution is one containing about 0.2 to 5 g thiourea/l having a pH generally ranging from about 1.8 to 2.4. Thiourea, however, is also effective over a pH range from 1.5 to 2.5.

EXAMPLE 7

Data were obtained on gold extraction in which the ore is biooxidized in accordance with the invention and was thereafter leached with a cyanide solution containing about 0.25 to 0.5 gpl of sodium cyanide at a pH of about 10. The solution may have up to about 5 gpl of sodium cyanide and the amount of cyanide may be dependent upon the amount of cyanide consumed by the biooxidized and neutralized ore.

Two types of ores were tested, one referred to as Newmont Post Mine and the other as Newmont Genesis Mine. Both ores were sulfidic non-carbonaceous ore.

The Post Mine ore contained by weight 2% barite, 1% jarosite, 5% kaolinite, 5% sericite, 2% pyrite and the balance substantially quartz (about 84%). The gold, sulfur and carbon contents were as follows: gold about 0.198 oz. (5,613 g per ton) per ton by fire assay, gold about 0.032 oz. per ton (0,907 g per ton) by cyanide assay, total sulfur about 1.61%, with sulfate sulfur about 0.38%, sulfide sulfur about 1.23%, total carbon about 0.23% of which 0.21% was acid insoluble, about 0.12% As, and iron about 1.68%.

The Genesis Mine ore contained 1% barite, 4% jarosite, 4% alunite, 13% kaolinite, 7% sericite, 2% arsenopyrite, 1% pyrite and the balance substantially quartz (over about 69%). The gold, sulfur and carbon contents were as follows: gold about 0.284 oz per ton (8,051 g per ton) by fire assay, gold about 0.083 oz. per ton (2,353 g per ton) by cyanide assay, total sulfur of 1.05%, with sulfate sulfur about 0.3%, sulfide sulfur about 0.75%, total carbon about 0.07% of which 0.02% was acid insoluble, about 0.51% As, and about 1.19% Fe.

Most of the gold was occluded in the ore since only 16% and 29% was cyanide soluble.

The mine samples of -1/2 inch size (-12,7 mm) were formed in particulates with an acidic solution of Thiobacillus ferrooxidans and biooxidized in columns comprised of 100 lbs. (45,36 kg) of ore for each column.

The Post Mine sample was biooxidized for a period of 210 days. The bacteria oxidized about 64% of the sulfide in the ore.

The results obtained are given in Table 5 below:

TABLE 5

| Gold Extraction from Refractory Sulfidic Ore Using Thiobacillus ferrooxidans Culture with Biooxidation in Columns | | | |
|---|----------------------------------|--------------------------------|-------------------|
| Ore Sample | Head Grade, oz Au/ton (z Au/ton) | CN leach ore residue oz Au/ton | Gold Extraction % |
| Post Mine sulfidic ore control | 0.196 (5,556) | 0.132 (3,742) | 32.6 |
| Post Mine sulfidic ore biooxidized | 0.201 (5,698) | 0.073 (2,069) | 63.7 |
| Genesis Mine sulfidic ore control | 0.284 (8,051) | 0.178 (5,046) | 37.1 |
| Genesis Mine sulfidic ore biooxidized | 0.284 (8,051) | 0.074 (2,097) | 73.9 |

In case of the Post Mine ore, the biooxidation increased gold recovery from 32.6% for the unbiooxidized ore or control to 63.7% for biooxidized ore.

With respect to the Genesis Mine ore, the biooxidation increased gold recovery from 37.1% for the unbiooxidized ore or control to 73.9% for the biooxidized ore.

Both tests confirm the advantages of heap leaching particulates of sulfide ore without the necessity of using costly equipment.

EXAMPLE 8

This example relates to the use of polymer agglomeration aids in the formation of stable ore particulates with *Thiobacillus ferrooxidans* culture and ore materials that include clay materials.

5 A 1% (by weight) suspension of NALCO 8877 poly(acrylamide) flocculant available from NALCO Chemical Company with 1-5 percent weight percent ethoxylated nonylphenol, 20-40 weight percent of hydrotreated light distillate along with sodium chloride and water was diluted to 0.1% (by weight) by adding 10 millimeters of the poly(acrylamide) suspension to 90 ml. of deionized water. The initial pH of the 0.1% solution was 7.31. The pH of that solution was adjusted to 2.00 by adding sulfuric acid.

10 A stock solution had previously been prepared containing a *Thiobacillus ferrooxidans* culture grown on a modified Kelly medium in the presence of iron having the following composition:

0.4 grams per liter ammonium sulfate

0.4 grams per liter magnesium sulfate heptahydrate

0.04 grams per liter dibasic potassium phosphate

15 33.3 grams per liter ferrous sulfate heptahydrate (pH adjusted to 1.8 with sulfuric acid.)

The stock culture solution had a *T. ferrooxidans* concentration of about 1×10^7 microorganisms per milliliter in modified Kelly medium (with iron.) Two milliliters of pH-adjusted 0.1% solution was then mixed with one milliliter of stock solution to form an agglomeration aid/inoculate solution. The resulting solution was clear and had a pH of 2.06. Upon microscopic examination using phase contrast microscopy at 1000X

20 magnification free bacterial cells were observed.

The ability of the polymer to maintain the integrity of an ore agglomerate was evaluated using plastic columns to emulate an ore heap. Each plastic column had a 45 mm. internal diameter and a 291 mm. length. A first specimen of 100 grams of sulfidic ore (-10 mesh) having the composition indicated in Table 6 was mixed with 10 milliliters of the agglomeration aid/inoculate solution.

TABLE 6

| Analyte | |
|-----------------------------------|---------------|
| Au,FA, (ounces per ton)(g/t) | 0.256 (7,257) |
| Au, CN, (ounces per ton) (g/t) | 0.012 (0,340) |
| AuPR value, (ounces per ton)(g/t) | 0.000 (0) |
| S-total % (wt) | 1.95 |
| S-SO ₄ , % (wt) | 0.54 |
| S-sulfide % (wt) | 1.41 |
| As, % (wt) | 0.1 |
| C-total, % (wt) | 0.33 |
| C-organic, % (wt) | 0.06 |
| AA/Fire ratio ¹ | 0.047 |

1 Atomic absorption to fire assay ratio

The sample is siliceous (80% quartz) and somewhat argillaceous, or clay-containing, (5% sericite, 7% kaolin). While it is pyritic (3% pyrite), there are also some iron oxides present (2% FeO_x), indicating the ore is partially oxidized. A second 100 gram specimen of the same ore was mixed with 10 milliliters of the stock culture solution alone for comparison purposes. Each specimen was then placed in a column to cure at room temperature for 24 hours with no solution circulating through the column. The ore height in the column containing the first ore specimen (treated with agglomeration aid and inoculate) had a height of 63 mm. and the column containing the second ore specimen (treated only with stock culture solution) had a height of 60 mm. Deionized water that had been acidified with sulfuric acid to a pH of 1.81 was circulated through each column. The flow rate of the column containing the first ore specimen was 20.3 ml. per minute and the flow rate for the column containing the second ore specimen was 21.0 ml. per minute. A clear difference was observed between the two columns. For the column that contained the first ore specimen a few fines were washed from the column, there was no apparent channelling and the flow through the column was slower

and some solution was apparent in the column above the sample at the specified percolation rate; whereas the column containing the second ore specimen exhibited both a large amount of fines being washed from the column and channelling. After approximately 5 hours the flow of acidified water was shut off and the column height was measured. The column height of the first ore specimen was 52 mm. (a 17.5% reduction) and the column containing the second ore specimen was 50 mm. (a 16.7% reduction).

The toxicity of the polymeric solution to *Thiobacillus ferrooxidans* was evaluated using a 0.1% stock agglomeration aid solution prepared as before. The pH of the solution was 2.0. A series of 9 further dilutions was made in accordance with Table 7 such that dilutions down to and including 10^{-10} percent were made.

TABLE 7

| SAMPLE | CONTENTS | POLYMER |
|--------|---|-----------------------|
| 1. | 10ml 0.1% Stock Polymer | $1 \times 10^{-1}\%$ |
| 2. | 9ml H ₂ O(pH 1.9) + 1ml of sample #1 | $1 \times 10^{-2}\%$ |
| 3. | 9ml H ₂ O(pH 1.9) + 1ml of sample #2 | $1 \times 10^{-3}\%$ |
| 4. | 9ml H ₂ O(pH 1.9) + 1ml of sample #3 | $1 \times 10^{-4}\%$ |
| 5. | 9ml H ₂ O(pH 1.9) + 1ml of sample #4 | $1 \times 10^{-5}\%$ |
| 6. | 9ml H ₂ O(pH 1.9) + 1ml of sample #5 | $1 \times 10^{-6}\%$ |
| 7. | 9ml H ₂ O(pH 1.9) + 1ml of sample #6 | $1 \times 10^{-7}\%$ |
| 8. | 9ml H ₂ O(pH 1.9) + 1ml of sample #7 | $1 \times 10^{-8}\%$ |
| 9. | 9ml H ₂ O(pH 1.9) + 1ml of sample #8 | $1 \times 10^{-9}\%$ |
| 10. | 9ml H ₂ O(pH 1.9) + 1ml of sample #9 | $1 \times 10^{-10}\%$ |

A double strength modified Kelly medium with iron, i.e., one having the formulation:

0.8 grams per liter ammonium sulfate
 0.8 grams per liter magnesium sulfate heptahydrate
 0.08 grams per liter dibasic potassium phosphate
 66.6 grams per liter ferrous sulfate heptahydrate

(pH adjusted to 1.8 with sulfuric acid) was prepared. A 5 milliliter aliquot of this double strength modified Kelly medium was placed in each of ten test tubes and 5 milliliters of diluted polymer solution as set forth for Samples 1 through 10 was added to each of these ten test tubes such that the first test tube had 5.0×10^{-2} percent polymer solution and so forth until the 10th test tube had 5.0×10^{-11} percent polymer solution. The 10 test tubes were then inoculated with 0.1 milliliter of *Thiobacillus ferrooxidans* stock culture solution prepared as before, mixed and incubated for three weeks or until activity occurred. Each of the ten test tubes exhibited the oxidation of ferrous iron and therefore metabolic activity, thereby demonstrating that the polymer was non-toxic to *Thiobacillus ferrooxidans* at concentrations of 1×10^{-1} to 1×10^{-10} percent concentration.

The ore to which the present invention is applicable includes metal sulfide ores containing up to about 3 to 5% sulfur substantially combined as sulfide sulfur, the amount of gold in the ore occluded in the metal sulfide being greater than about 0.02 oz. per ton (0.56 g per ton) of ore, and generally greater than about 0.05 oz. per ton (1.41 g per ton) of ore.

Other and specific ores advantageously treated in accordance with the described process are: Gold Quarry sulfidic ore; Gold Quarry sulfidic-carbonaceous ore (requires coupling biooxidation with carbon deactivation process), Post Deposit sulfidic ore; Genesis Deposit sulfidic ore; Carlin Deposit sulfidic ore; Pete Deposit sulfidic ore; Salave sulfidic ore; Kirazli sulfidic ore; Atlanta Gold Deposit sulfidic ore; Homestake McLaughlin refractory sulfidic ore; and, ores from which bioleaching of metal values could be facilitated by the bioleach-heap process.

Amongst the ores specific candidate ores, the following typical ores are illustrative:

TABLE 8

| Minerology of Candidate Ores | | | |
|------------------------------|--------------|-------------|------------|
| Element | A | B | C |
| Gold, oz/ton (g/t) | 0.55 (15,59) | 0.26 (7,37) | 0.11(3,11) |
| Sulfide, % | 4.14 | 3.33 | 1.66 |
| Iron, % | 3.51 | 3.48 | 3.62 |
| Arsenic, % | 5.34 | 0.18 | 0.47 |
| Carbonate, % CO ₂ | 0.45 | 0.29 | 1.50 |
| Graphitic Carbon, % | 0.27 | 0.83 | 0.11 |
| Silica, % | 56.9 | 76.2 | 61.7 |

For purposes of illustration for forming particulates of the type as schematically shown in Figure 2 above, Table 9 below is presented for two ores. It is to be understood that ultimately the proper particle size is that which functions best for each particular ore of its specific mineralogy for a) forming particulates and b) providing the most economical results for biooxidation and precious metal recovery. However, the present method description has provided one with a prescription of how to use properly an ore for forming a particulate with an agglomeration aid and/or with bacterial solution.

TABLE 9

| Ore Particle Size Distribution for Samples Used for Testing the Biooxidation-heap Pretreatment System | | | | | |
|---|----------------|----------|----------------------|----------------|----------|
| Size (inch = 25,4mm) | Weight Percent | | Size (inch = 25,4mm) | Weight Percent | |
| | Sample A | Sample B | | Sample C | Sample D |
| + 1.5" | 17.70 | 14.66 | + 1" | 7.93 | 27.2 |
| 1.5 + 1" | 28.68 | 24.71 | -1 + 3/4" | | 12.0 |
| -1 + 3/4" | 11.57 | 11.14 | -1 + 1/2" | 67.37 | |
| -3/4 + 1/2 | 10.11 | 10.70 | -3/4 + 1/2 | | 12.3 |
| -1/2 + 1/4 | 12.13 | 14.38 | -1/2 + 1/4 | 16.91 | 16.3 |
| -1/4" + 10 mesh | 11.25 | 14.54 | -1/4" + 10 mesh | 5.07 | 16.3 |
| -10 mesh | 8.56 | 9.87 | -10 mesh | | 15.9 |
| | | | -10 mesh + 35 mesh | 0.95 | |
| | | | -35 mesh | 1.77 | |
| A = Gold Quarry sulfidic-carbonaceous ore B = Gold Quarry sulfidic-carbonaceous ore C = Gold Quarry sulfidic-carbonaceous ore D = Post Mine sulfidic ore | | | | | |

Refractory sulfidic-carbonaceous ores, typical of the Gold Quarry deposit, are amenable to biooxidation to expose the sulfide occluded gold. However, the presence of the acid-insoluble ("organic") carbon, prevents economic recovery of the gold by cyanide leaching because of the affinity of the carbon for the gold-cyanide complex. Following biooxidation, the carbon must be deactivated to facilitate the cyanide leach of the gold. Because thiosulfate or thiourea lixivants are less affected than cyanide by the organic carbon present in the ore, alternatively gold can be leached from the biooxidized sulfidic-carbonaceous ores with these lixivants.

Kerosene is an agent which can "blind" the carbon surface to prevent adsorption of the gold-cyanide

complex. The ore can be treated with kerosene, up to two gallons kerosene/ton ore, following the biooxidation step and preceding cyanidation. The carbon becomes sufficiently deactivated for improved extraction (e.g., from about 40% without kerosene to about 70% with kerosene) of gold with cyanide.

Surfactant blinding of the carbon reacts in a similar fashion to kerosene blinding. Certain anionic surfactants have carbon deactivation capability.

Hypochlorite (bleach) can also be used to deactivate the gold-sorbing carbon in ore following biooxidation. Cyanide extraction of gold can be increased from about 40% without hypochlorite to about 80% following hypochlorite treatment. However, there can be a very high consumption of the reagent hypochlorite, up to several hundred pounds/ton ore, if the sulfide is not completely oxidized. The more effective the biooxidation of the sulfide, the lower the hypochlorite consumption.

The preparation of the *Thiobacillus ferrooxidans* for the agglomeration/inoculation of the ore was done on site. A strain of the microbe was first grown at a laboratory. Three 50-gallon (227 l) batches of the culture were then transported to the test site for inoculation of a solution in the culture preparation tanks.

Three 500-gallon (2270 l) tanks, each with a diffuser-aerator, contained about 360 gallons (1636 l) of the nutrient medium (previously described in the patent above) at an initial pH 2.2. Each tank was inoculated with the 50-gallons (227 l) of *T. ferrooxidans* culture. Each tank was aerated (90 standard-cubic-feet/hour) using compressed air. The bacteria oxidized 98% to 99% of the ferrous iron during the first four days of incubation.

The bacterial culture from the respective 500-gallon (2270 l) tanks was used to inoculate three 5000-gallon (22700 l) tanks containing about 3600 gallons (16365 l) of nutrient medium. Each tank was aerated. Following two days incubation, 93% to 98% of the ferrous iron was oxidized. The three 4000-gallon (18184 l) batches of the culture were used for the biooxidation-heap test.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

Claims

1. In a process for biooxidation of sulfides in a heap of mineral ores, comprising metals dispersed or occluded within said ores as pyritic or arsenopyritic sulfides and the like, the improvement comprising :
 - forming particulates from ore particles with an inoculate comprising bacteria capable of attacking, by biooxidation, said sulfides and/or elemental sulfur and ferrous iron in said ore particles;
 - constructing a heap of said particulates;
 - biooxidizing said sulfides and/or sulfur and ferrous iron in said body constructed of said particulates wherein said biooxidation is aided by a formation of ferric and other ions in a leaching solution dispersed within said heap;
 - circulating said leaching solution within said heap;
 - and
 - recovering said metal values from said heap.
2. In a method for biooxidation of sulfides of pyritic and like nature in an ore body comprising precious metals, wherein said precious metals are dispersed or occluded within said sulfides, the improvement comprising:
 - forming particulates from crushed ore particles with an inoculate comprising bacteria capable of attacking, by biooxidation, said sulfides and/or elemental sulfur and ferrous iron;
 - biooxidizing said sulfides and/or sulfur and ferrous iron in an ore body constructed of said particulates wherein said biooxidation is aided by a formation of ferric and other ions in a solution dispersed within said ore body;
 - recovering soluble excess metal values from said solution; and
 - recovering said precious metal values from said ore body.
3. In a method for biooxidation of sulfides of pyritic and arsenopyritic nature in mineral values in a heap forming an ore body wherein said mineral values include precious metal values dispersed or occluded within said sulfides, the improvement comprising:
 - crushing said mineral values to form ore particles of a preselected particle size;
 - forming particulates of said particles by admixing thoroughly said particles with an inoculate solution comprising bacteria capable of attacking, by biooxidation, said sulfides and/or elemental sulfur

- and ferrous iron;
 constructing a heap of said particulates;
 maintaining said heap favoring bacterial growth within and on said particulates;
 biooxidizing said sulfides and/or sulfur in said ore particles in said heap constructed of said
 5 particulates;
 aiding further said biooxidation by introduction of inoculate solution in said heap;
 circulating continuously said inoculate solution within said heap;
 recovering soluble excess metal values from said solution primarily of ferric ion or arsenate ion
 species;
 10 reconstituting said heap of said particulates conjointly with lime, Portland cement, cement, dust or
 sodium hydroxide addition for neutralization of acidic materials in said particulates; and
 recovering said precious metal values from said heap by cyanidation or a thiosulfate treatment of
 said neutralized, reconstituted particulates.
- 15 4. A process for biooxidation of sulfide values in a precious metal containing ore comprising the steps of:
 constructing particulates from a crushed form of said ore, ore slimes and like particles of said ore
 of predetermined size, surface area and bacterial inoculant content;
 forming a heap of said particulates;
 biooxidizing said particulates for a time sufficient to biooxidize sulfide values in said particulates to
 20 make amenable said precious metal in said ore to cyanide, thiourea or thiosulfate leaching;
 and
 recovering precious metal values from said biooxidized particulates.
5. A process for the recovery of one or more metal values from a metal ore material in the presence of
 25 clays and/or fines
 material, said ore material being comprised of one or more metal values and a matrix material having a
 sulfur content wherein sulfur is present in an oxidation-reduction state of zero or less, said process
 comprising forming particulates from particles comprising said ore material, particles comprising said
 clays and/or fines material, an acid-resistant polymeric agglomeration aid and an inoculate comprising
 30 bacteria capable of at least partially biooxidizing the sulfur content; forming a heap of said particulates;
 biooxidizing the sulfur content and recovering one or more metal values from said ore material.
6. The process as defined by claim 1 wherein said forming comprises pretreating said particles to reduce
 their pH.
- 35 7. The process as defined by claim 1 wherein the process further comprises forming said particulates in
 the presence of an acidic material.
8. The process as defined by claim 1 wherein the process comprises treating said particulates to acidify
 40 them after forming said particulates.
9. The process as defined by claim 5 wherein said forming comprises treating said particles with said
 agglomeration aid concurrently with treating said particles with said inoculate.
- 45 10. The process as defined by claim 9 wherein said forming further comprises pretreating said particles to
 acidify them before treating with said agglomeration aid.
11. The process as defined by claim 9 wherein said forming further comprises treating said particles to
 acidify them concurrently with treating with said agglomeration aid.
- 50 12. The process as defined by claim 9 wherein said forming further comprises treating said particles to
 acidify them after treating with said agglomeration aid.
13. The process as defined by claim 5 wherein said forming comprises treating said particles with a
 55 solution comprising said agglomeration aid and said inoculate.
14. The process as defined by claim 13 wherein said forming further comprises pretreating said particles to
 acidify them before treating with said agglomeration aid.

15. The process as defined by claim 13 wherein said forming further comprises treating said particles to acidify them concurrently with treating with said agglomeration aid.
16. The process as defined by claim 1 wherein said forming comprises treating said particles with an acid solution to acidify them, said solution comprising said agglomeration aid and said inoculate.
17. The process as defined by claim 16 wherein said agglomeration aid comprises an acid-resistant, microbial biooxidant-compatible, water-soluble vinyl addition polymer material.
18. The process as defined by claim 17 wherein the acid-resistant, microbial biooxidant-compatible, water-soluble vinyl addition polymer material comprises polymers, copolymers, terpolymers and higher polymers of a compound having the general formula
$$C=C-R$$
where R is a nitrile, an amide, a carboxyl radical, COOR¹ wherein R¹ is a lower alkyl radical having from 1 to 4 carbon atoms, and the water-soluble salts thereof.
19. The process as defined by claim 18 wherein the acid-resistant, microbial biooxidant-compatible, water-soluble vinyl addition polymer material comprises a homopolymer of an acrylamide; a homopolymer of an acrylic acid; a copolymer, terpolymer or higher polymer of an acrylamide and at least one monomer other than an acrylic acid; a copolymer, terpolymer or higher polymer of an acrylic acid and at least one monomer other than an acrylamide; a cationic or nonionic copolymer of an acrylamide and an acrylic acid; and a terpolymer or higher polymer of an acrylamide, an acrylic acid and at least one other monomer and wherein said acid resistance is based on a waste heap leaching of an ore particulate for at least 3 weeks.
20. The process as defined by claim 17 wherein the acid-resistant, microbial biooxidant-compatible, water-soluble vinyl addition polymer material comprises a polyacrylamide.
21. The process as defined by claim 17 wherein the acid-resistant, microbial biooxidant-compatible, water-soluble vinyl addition polymer comprises a moderately anionic polyacrylamide, a cationic polyacrylamide or a nonionic polyacrylamide.
22. The process as defined by claim 1 the bacteria are selected from *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, *Thiobacillus organoparus*, *Thiobacillus acidophilus*, *Leptospirillum ferrooxidans*, *Sulfobacillus thermosulfidooxidans*, *Sulfolobus acidocaldarius*, *Sulfolobus BC*, *Sulfolobus solfataricus*, *Acidanus brierleyi* or a mixture thereof.
23. A heap comprising a plurality of particulates of an ore material having one or more desired metal values and a matrix material having a sulfur content wherein the sulfur is present in an oxidation-reduction state of zero or less, each particulate comprising a core particle of said ore material and a size of less than about two inches and a layer of particles comprising said ore material particles and said clays and/or fines material, an acid-resistant polymeric aggregation aid and an inoculate of sulfur-biooxidizing bacteria in admixture with said particles wherein said particulate has sufficient strength to retain at least about 95% of a void volume for a column height of about 6 feet for at least 200 days when continuously bathed in a solution comprised of said inoculate or a nutrient therefor.
24. The heap as defined by claim 23, wherein a core of said heap is constructed of particulates with a bacterial inoculant of *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, *Thiobacillus organoparus*, *Thiobacillus acidophilus*, *Leptospirillum ferrooxidans*, *ferrooxidans*, *Sulfobacillus thermosulfidooxidans*, *Sulfolobus acidocaldarius*, *Sulfolobus BC*, *Sulfolobus solfataricus*, *Acidanus brierleyi* or a mixture thereof.

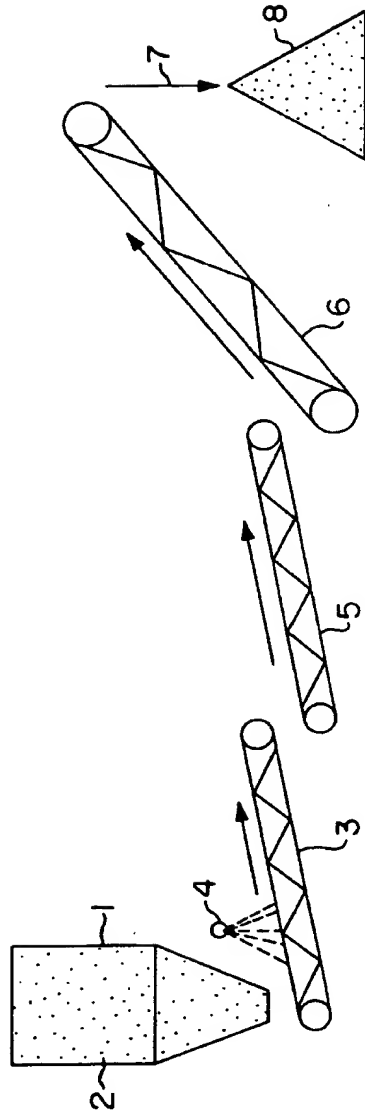


FIG. 1

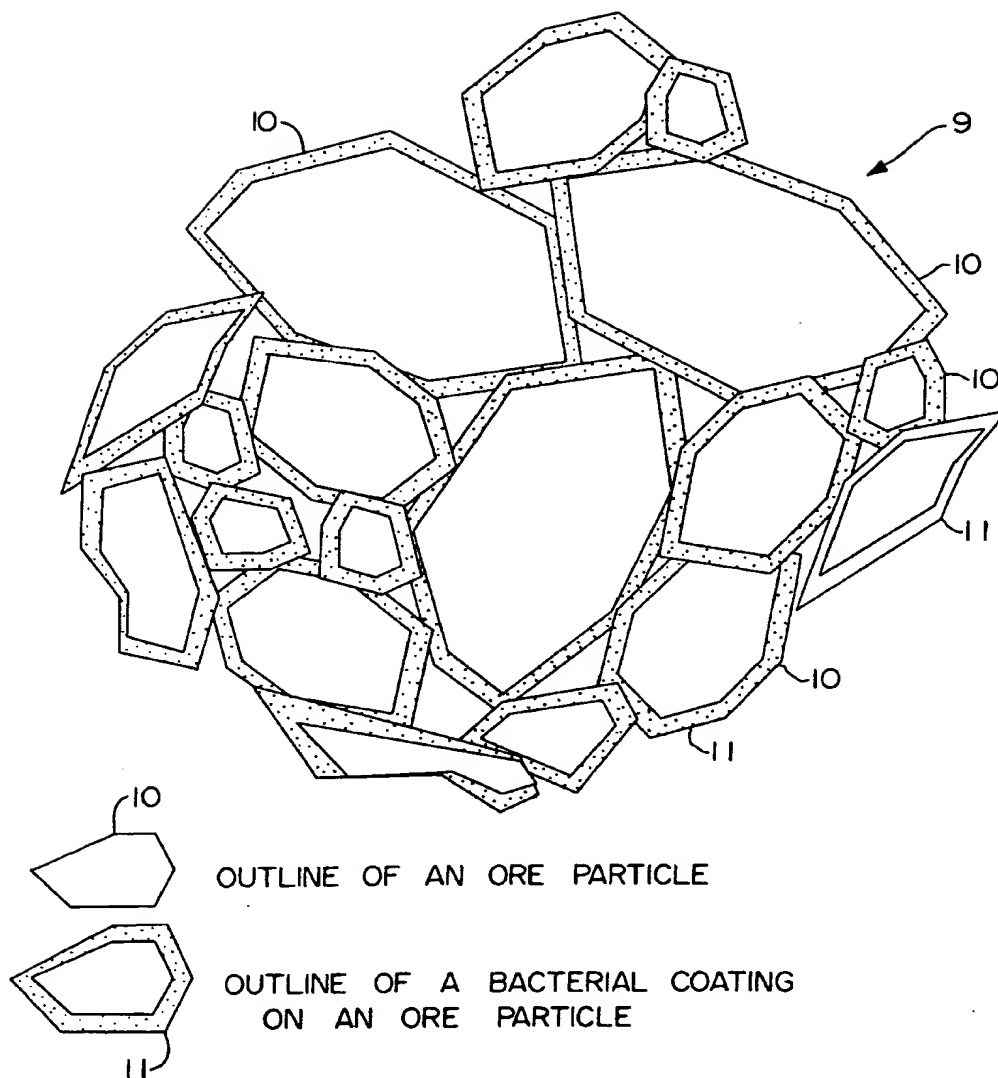
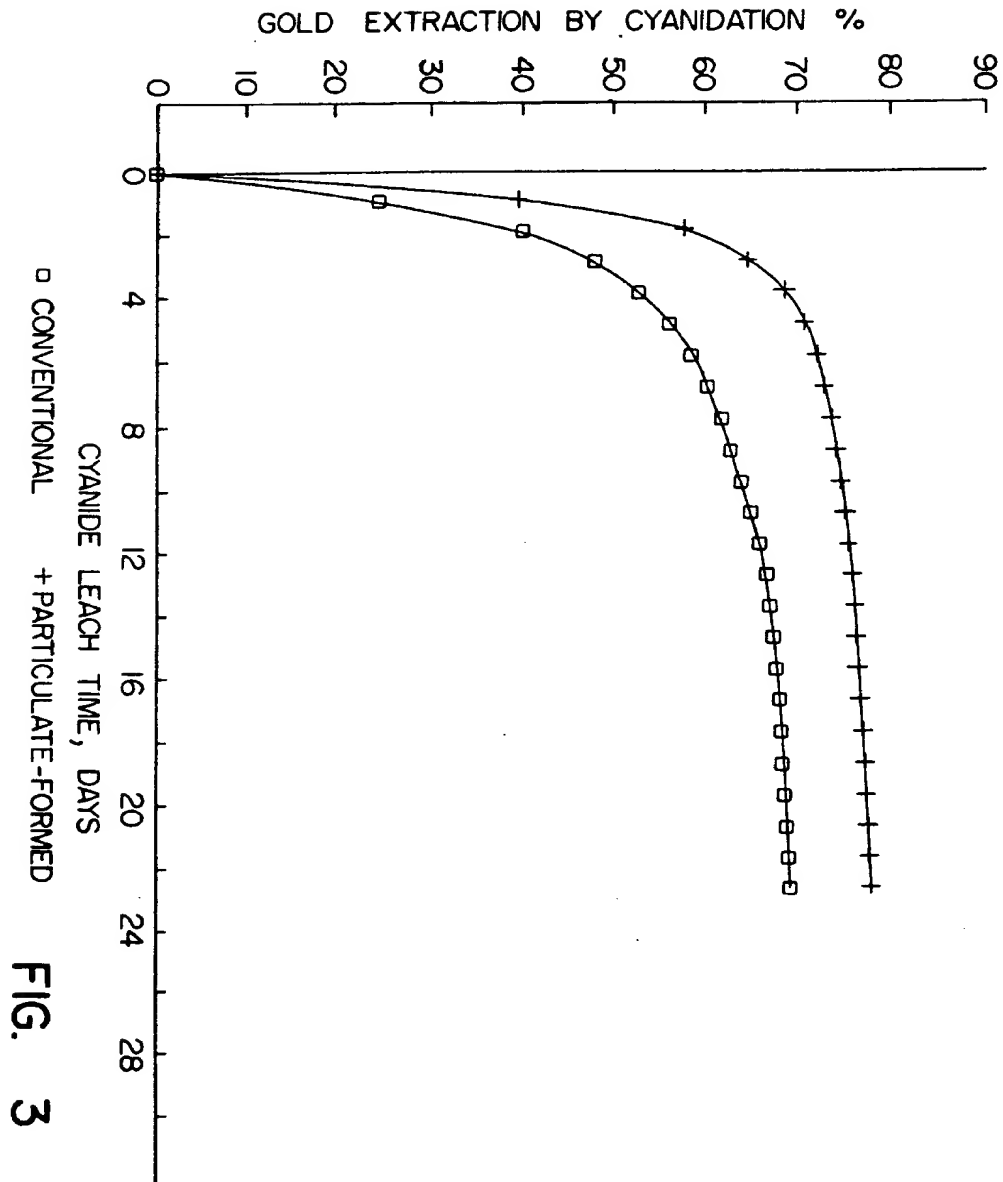


FIG. 2



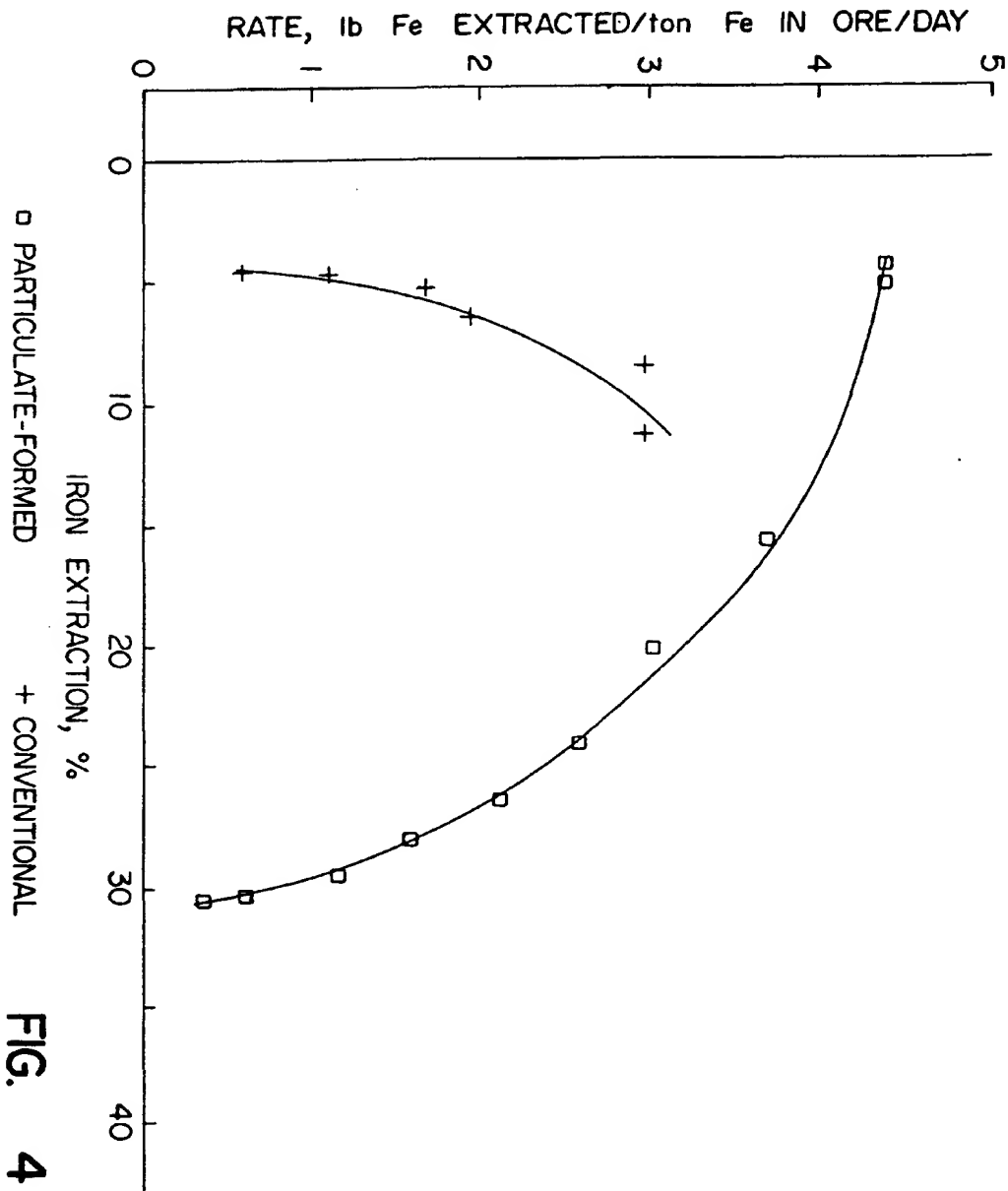


FIG. 4

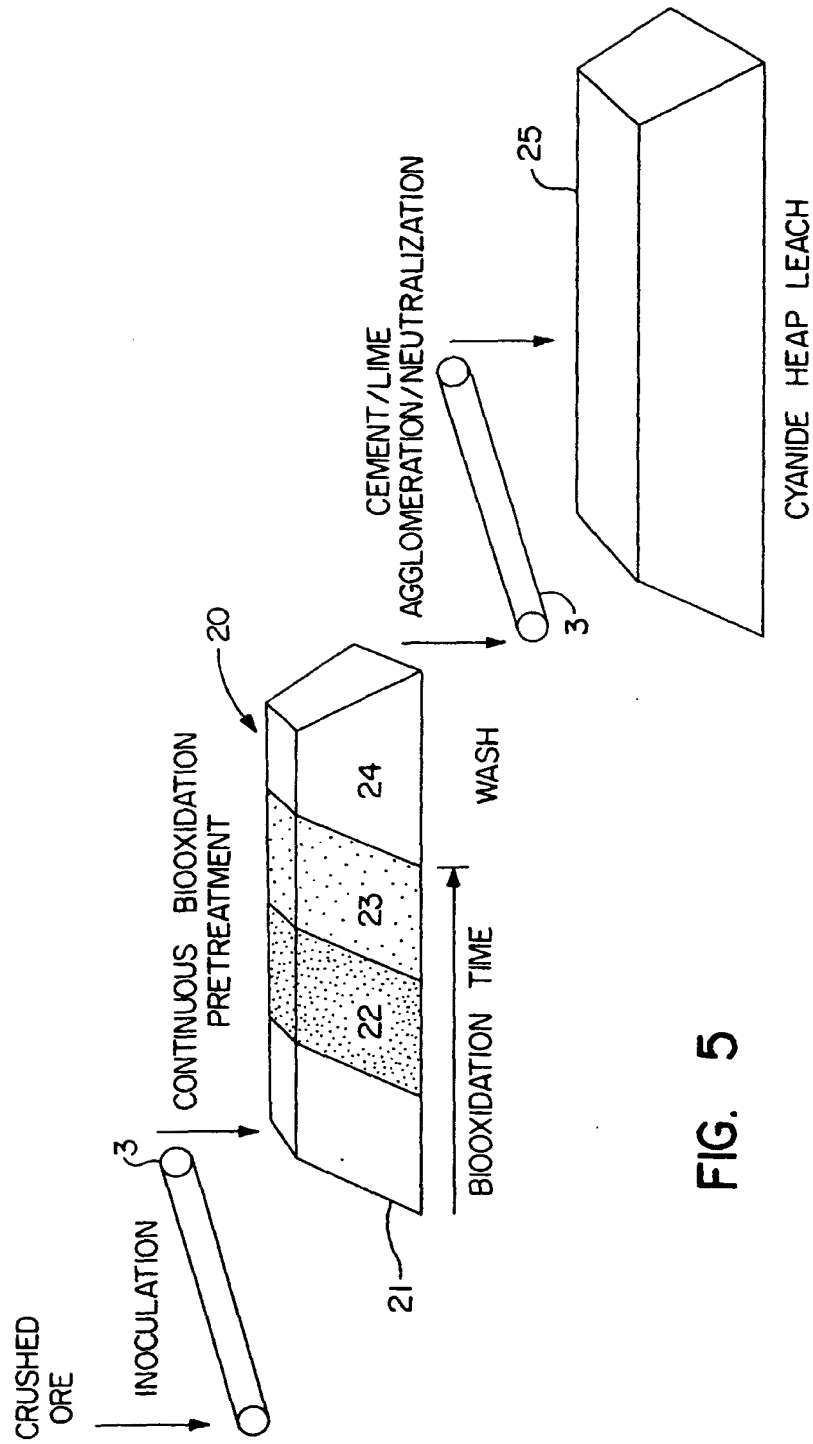


FIG. 5

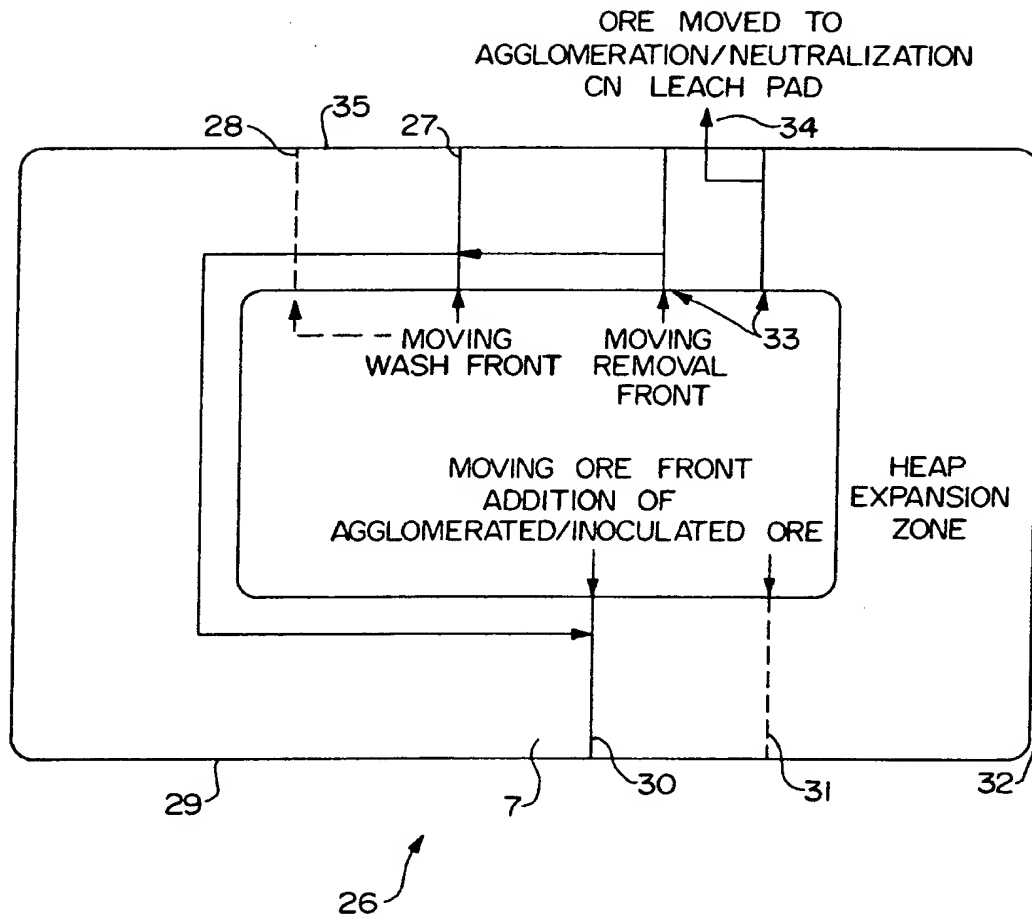


FIG. 6

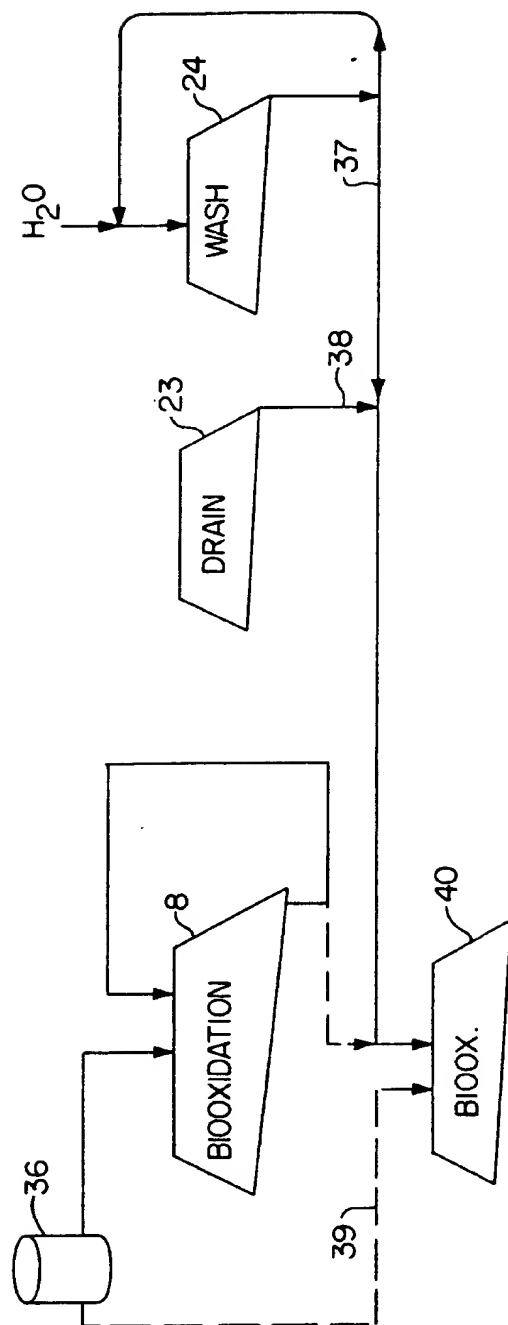


FIG. 7



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 40 2026

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|---|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. CL.5) |
| Y,D | US-A-4 875 935 (A. E. GROSS ET AL.) * column 4, line 31 - line 32; claim 1 * | 1 | C22B3/18 |
| Y | GB-A-2 180 829 (AUROTECH N.L.) * claim 1 * | 1 | |
| A,D | US-A-4 256 706 (H. J. HEINEN ET AL.) * claim 1 * | 1 | |
| A,D | US-A-4 374 097 (L. D. HOLLAND) * claim 1 * | 1 | |
| A,D | US-A-4 898 611 (A. E. GROSS) * claim 1 * | 1 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. CL.5) |
| | | | C22B |
| The present search report has been drawn up for all claims | | | |
| Place of search BERLIN | | Date of completion of the search 19 OCTOBER 1992 | Examiner SUTOR W. |
| CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document | | | |